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WATER POLLUTION POTENTIAL OF COAL-SLURRY PIPELINES

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16. ABSTRACT

Coal is expected to assume an increasingly important role in meeting America's energy needs during the remainder of this century and, perhaps, to become the principal source of energy during the next. It has been predicted that coal production will double during the next decade, with much of the increase coming from low sulfur deposits in the West. The economics of using coal is dependent in large measure on the economics of transporting it, since shipment costs can amount to as much as two-thirds of the delivered price. Coal-slurry pipelines have been proposed as one economical means of transporting coal over long distances to specific markets.

This report characterizes those contaminants associated with transport waters from coal-slurry pipelines. This was accomplished through tests using a rotating bench scale reactor. Tests consisted of coal mixed with (1) tap water, (2) tap water with additives, (3) synthetic saline water, and (4) synthetic saline water with additives. Tests were performed for a period of 12 days each.

The results of the research will be useful to pipeline planners and regulatory agencies as a preliminary tool to assist them with decisions regarding slurry water quality, water reuse possibilities, and treatment and utilization options for spent slurry liquids.

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FOREWARD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report characterizes those contaminants associated with transport waters from coal slurry pipelines. This was accomplished through tests using a rotating bench scale reactor. The results of this research should be useful for pipeline planners and regulatory agencies as a preliminary tool to assist them with decisions regarding slurry water quality, water reuse possibilities, and treatment and utilization options for waste slurry liquid. For further information, contact the Energy Pollution Control Division.

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ABSTRACT

Coal-slurry pipelines have proven to be a reliable and economical means of transporting coal over long distances to specific markets. At the pipeline terminus, large volumes of water must be separated from the coal. Experiments at Montana State University which modeled coal-slurry systems indicated that some chemical interaction between coal and transport water will occur in the pipeline. Fresh water will experience an increase in total dissolved solids while the TDS of saline water decrease. Analysis of coal samples prior to and after the experiment indicated that the material lost from the water remained on or with the coal.

Conclusions can be drawn that saline water is not a satisfactory transport medium since it increases the mineral content of the coal which would produce greater quantities of fly ash and exacerbate corrosion of furnace components. Dissolution of minerals and organics in initially fresh transport water will limit its usefulness in the power plant and will probably necessitate treatment prior to reuse and/or discharge. Removal of the dissolved organics, or use of algalcides other than chlorine will be necessary to prevent formation of haloform compounds.

This report was submitted in fulfillment of Contract No. R-805176-01 by Montana State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 1, 1978 to September 30, 1980, and work was completed as of December 12, 1980.

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SECTION 1

INTRODUCTION

Coal is expected to assume a greater role in meeting America's energy needs during the remainder of this century and, perhaps, to become the principal source of energy during the next century. It is anticipated that coal production in the United States will increase drastically during the next decade, with much of the increase coming from low sulfur deposits in the west. The economics of using this coal is dependent, in large measure, on the economics of transporting it. Since major markets are hundreds of miles away from western coal deposits, shipment costs can amount to as much as two-thirds of the delivered price of the coal (Blazek, 1975; Palmer and others, 1977). Coal-slurry pipelines have been proposed as one economical means of transporting coal over long distances to specific markets.

Considerable attention has been given to the economic, environmental, and social impacts of coal-slurry pipelines versus the impacts of conventional methods of transporting coal or energy derived from coal. Even a summary of the available information would be too voluminous for inclusion in this report. However, it is generally conceded that, with regard to environmental factors a coal-slurry pipeline would compete favorably with other forms of coal transportation.

There is, however, one potentially important aspect of slurry pipelines that has received very little attention. This involves the quality of the transport water after it has been separated from the coal at the pipeline terminus. Although this water ultimately is expected to be put to use in the power plant that uses the coal, some of this water is likely to become a waste discharge to the environment.

The quality of the water after separation will be an important factor in determining both the use to which it can be put and the conditions under which it can be discharged. Economics of treatment of this water, either for use or for discharge, could be an important consideration in the evaluation of coal-slurry pipeline projects.

Until this time little information has been available on this subject. In an attempt to provide this much needed information, a project investigating the chemical interactions of water and coal in coal-slurry pipelines has been conducted at Montana State University (MSU). The objective of the MSU project was to determine the type and amount of inorganic and organic contaminants that can be expected to remain in the water after its use as a transport medium in a coal-slurry pipeline.

Coal-slurry pipeline conditions were simulated as closely as possible in both pilot plant and laboratory facilities. Intermittent samples were drawn, separated, and tested for a variety of chemical constituents. This report summarizes available literature on the subject of chemical interaction of water and coal in slurry systems, describes the equipment and procedures used in the MSU study, and presents the results of that study.

SECTION 2

CONCLUSIONS

Based on the results of this study, the following conclusions are reached.

1. Chemical interactions do occur between water and coal under simulated conditions of coal-slurry pipelines. Although these interactions do not result in gross pollution of the transport medium, water quality impairment, with respect to some parameters may be significant.

2. Chemical interactions between the water and the coal used in this study (Rosebud Seam, Fort Union Formation) result in:

   a. A decrease in pH of approximately two units (from approximately 8 to approximately 6). Dissolution of metals at a pH of 6 was not significant.
   b. Increased mineral content of fresh water. Alkalinity, total dissolved solids (as indicated by electrical conductivity), and sulfates show several-fold increases. Use of phosphorus-based chemical additives for corrosion control result in substantial concentrations of phosphate.
   c. Turbidity remains in the water after separation of the coal by centrifugation. Although some color may be present as a result of humic acids and manganese, colloidal particles appear to be the main cause of turbidity.
   d. Dissolved organic carbon levels that may be significant if reuse (either prior to or after discharge) requires chlorination. These organics are potential precursors of chlorinated hydrocarbons.

3. Saline water as a transport medium should be avoided if possible. However, pipeline construction in water short areas may necessitate the use of saline water. Saline water poses reuse/discharge problems and results in significant amounts of metallic salts accompanying the coal after slurry separation.

4. Treatment of the transport water may be necessary to:

   a. reduce mineral content
   b. reduce turbidity
   c. avoid formation of chlorinated hydrocarbons

Both the type and the extent of treatment will be dependent on the nature of reuse/discharge. Wastewater treatment technology is currently available to reduce concentrations of all the contaminants reported in this study to practically any level desired. Removal of the dissolved constituents may be expensive.

SECTION 3

RECOMMENDATIONS

Based upon our findings, we offer the following recommendations.

1. The transportation of coal over long distances via coal-slurry pipelines is a proven technology. Simplicity of operation and low labor intensity make this an attractive alternative to operators of coal-fired power plants, coal gasification plants, and coal liquefaction facilities. The Environmental Protection Agency should begin preparations now to establish effluent guides for discharge of transport water from coal-slurry operations. Additionally, procedures for reevaluating effluent guidelines for other waste streams within the user industry to which transport water may be added prior to discharge should also be established.

2. Two areas that should be further researched immediately are:

   a. The dissolution of metals in low pH systems, which would be likely to occur if high sulfur coal from eastern regions of the US were slurried.
   b. The formation of carcinogenic, or potentially carcinogenic, compounds upon chlorination of coal-slurry wastewater.

SECTION 4

BACKGROUND INFORMATION

COAL-SLURRY PIPELINE OPERATIONS

The technology for coal-slurry pipelines is well established. As early as 1891, a patent was granted for pumping pulverized coal in a fluid medium (Bechtel, Inc., 1976). The first pipeline of the type being used today was built in England and operated from 1914 to 1924 to transfer coal from barges in the Thames River to a power plant some 600 m away (Doughterty, 1951; McNamara, 1961). The first coal-slurry pipeline in the U.S. was constructed between Cadiz and Cleveland, Ohio, a distance of 175 km, and operated from 1958 to 1963 when lower railroad freight rates were negotiated (Dauber, 1957; Bender, 1963; Bechtel, Inc., 1976). The second pipeline, from Black Mesa, Arizona, to Mohave, Nevada, began operation in 1970 and has operated almost continuously since. The 440 km, 45 cm diameter line carries approximately 5 million metric tons per year over a very uneven terrain (Dina, 1976).

The success of the Black Mesa pipeline has encouraged other coal-slurry projects (Erker, 1977; "Coal Slurry Pipelines," 1974; "Two-Hundred-Seventy-Mile Pipeline," 1968; Davis, 1976; Bechtel, Inc., 1976). Several pipelines that are in various stages of planning are shown in Figure 1. Should legislation be passed that gives eminent domain to slurry pipelines, and should water sources become available, it is likely that these and many more pipelines will be constructed.

Coal-slurry pipeline operations consist of mine-mouth preparation of the coal, the actual pumping of the slurry through the pipeline, and, finally, dewatering at the pipe terminus. These operations are shown graphically in Figure 2.

Slurry preparation consists of dry-crushing the coal to approximately 6 mm in diameter and then wet-grinding to the desired specifications. Normally, these specifications require that 100 percent of the coal must pass the no. 14 sieve (1.2 mm diameter) and that not more than 20 percent of the coal may be retained on the no. 325 sieve (0.04 mm diameter)(Bernstrom, 1977). Enough water is then added to the pulverized coal to make a fluid mixture. The actual water content of the slurry will vary with different coals. A ratio of 50/50 by weight is a figure commonly assumed for pumpable slurries, but pumpable slurries may range as high as 60 percent coal to 40 percent water on a dry-weight-of-coal basis (Bender, 1963; Lansing, 1957).

After water and coal have been mixed, the slurry is then fed into the pipeline by a pumping plant. Intermediate pumping stations may be necessary to maintain sufficient pressure to ensure adequate velocity. Velocities of at least 1.2 m/sec are required to keep the particles in suspension. Pumping station spacing will vary depending on several factors; a range of 80 to 240 km is common. Auxiliary facilities at each pumping station may include dump ponds that can hold the contents of the line between stations should draining the line become necessary.

Facilities at the pipe terminus include storage tanks and dewatering equipment. Storage tanks should be sized to maintain operations for a reasonable length of time while the pipeline is shut

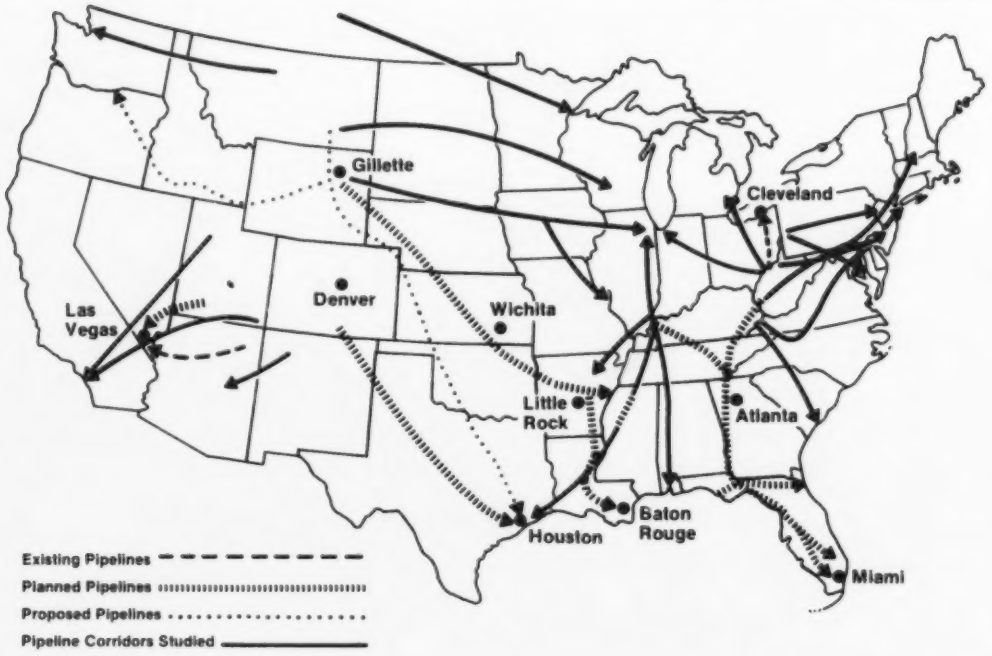

Figure 1. Existing and Proposed Coal-slurry Pipelines
(Courtesy of Slurry Transport Association, Washington, D.C.)

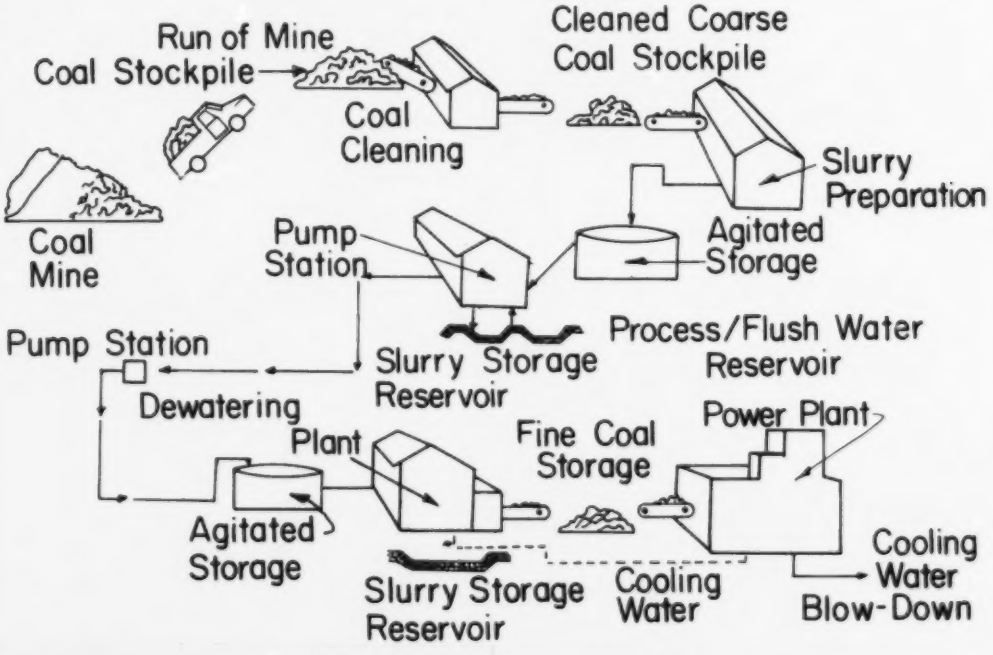

Figure 2. Coal-slurry System

down for repairs or routine maintenance. Dewatering is usually accomplished by centrifugation, although microscreening and other separation techniques could be employed. From 30 to 40 percent of the slurry water will remain on the coal and accompany it to the furnace. The remaining 70 to 60 percent of the water is recovered and must be disposed of in an acceptable manner.

Operating experience has not provided any information with regard to the discharge of wastewaters which contain transport water. The Black Mesa Pipeline terminates at the Mohave Power Plant in the southern Nevada desert. Wastewaters from the power plant are sent to evaporation ponds where a net evaporation rate of 1.7 m/year eliminates any surface discharge. Consequently there is no discharge to surface waters.

Most of the proposed pipelines terminate in high rainfall areas. In the Houston, Texas, area, evaporation exceeds rainfall by only 18 cm per year; therefore evaporation would require exceedingly large ponds. Land is simply not available for evaporation ponds of this size. In the Little Rock, Arkansas, area, rainfall exceeds evaporation by 15 cm per year, making evaporation ponds unworkable under any circumstances.

When evaporation is not practical, several possibilities exist for disposal of transport water. The most commonly mentioned applications are (1) recycling for use in slurry transport, (2) utilization by the power plant receiving the coal, and (3) agricultural irrigation. While attractive from an environmental and water conservation standpoint, recycling is not an economically viable alternative at the present time. The additional capital cost of installing dual facilities and the operating cost of pumping water several hundred miles up hill would make slurry pipelines non-competitive in today's market ("Coal Slurry Pipelines . . .," 1974; Butler, 1976).

Most coal-slurry pipeline promoters advocate using the separated water in the power plant operations at the pipeline terminus. The most common proposal is to use it as a part of the makeup water for cooling towers. To prevent mineral solids buildup, portions of the cooling tower water must be removed and replaced. Thus, portions of the transport water must eventually become wastewater, and a knowledge of the quality of this water becomes important.

If the slurry water has come from a saline aquifer, it would not be suitable for agricultural irrigation without rather extensive treatment. Even if the slurry water was generally acceptable for irrigation before it was used as a transport medium, the use of recovered slurry water for agricultural irrigation is probably not feasible, because of high levels of total dissolved solids (TDS) (400 to 1,100 mg/l) (Office of Technology Assessment, 1978).

CHEMICAL INTERACTIONS BETWEEN WATER AND COAL

The chemical interactions between water and coal in coal-slurry pipelines have not been previously documented. There is, however, considerable information available that should be of assistance in predicting the nature of the interactions that are likely to occur. For instance, information on the chemical nature of coal, the chemical nature of the water used as a transport medium, and potential reactions between the chemical constituents of each should provide clues about probable interactions and end products. This section of the report will identify the constituents of coal and water and indicate the probable reactions that should be of interest in a study of coal-slurry pipelines.

The Nature of Coal

Coal is a mixture of both organic and inorganic substances. The organic substances have been derived primarily from vegetative matter, the exact structure of which varies with many factors. The

basic building blocks for all coals were the lignin and cellulose of the original plants, and the variability of the original organic matter is reflected in the different classifications of coal, such as brown coal, lignite, subbituminous, bituminous, anthracite, etc. (Peck, 1961).

Inorganic matter in coal is commonly referred to as mineral matter. Mineral matter may be termed "inherent" or "extraneous" depending on its origin. Inherent mineral matter had its origin in the vegetative matter that eventually became coal. Extraneous mineral matter entered the coal from non-plant origins. The principal separable impurities of most coals are of the extraneous type (Lowry, 1945; Lincoln, 1913; O'Donnell and Sprunk, 1942; Headlee and Hunter, 1953).

Major categories of mineral matter commonly found in coal include aluminosilicates, sulfur compounds, carbonates, and silica (O'Donnell and Sprunk, 1942; Babu, 1975). Aluminosilicates, usually the largest fraction of the mineral matter in coal, consist of clays such as kaolinite, montmorillonite, and illites. These substances are extraneous in nature and were probably deposited with the vegetative matter in the peat stage of coal formation, or perhaps entered with percolating waters and were deposited in cracks of the coal formation.

Sulfur is a ubiquitous constituent of coal, ranging from 0.2 to 10 percent by weight, depending on the location of the coal beds (Boulding, 1976). Generally, coal is classified according to sulfur content as follows (DeCarlo and others, 1966):

Low sulfur	< 1.0%
Medium sulfur	1.0-3.0%
High sulfur	> 3.0%

Inorganic sulfur compounds can be sulfides or sulfates. The most common are pyrite (FeS_2 cubic crystals), marcasite (FeS_2 orthorhombic crystals), sphalerite (ZnS) and galena (PbS). These compounds may be oxidized to sulfate forms if oxygen is present. These inorganic forms of sulfur are extraneous minerals which were left in joints and fractures of coal deposits by percolating waters. Usually an inherent mineral, organic sulfur was a part of the vegetation which ultimately became coal and thus has a more or less uniform distribution throughout the coal. Organic sulfur is often found in reduced forms such as mercaptans.

Carbonate is an extraneous mineral. The predominate forms of carbonate in coals are calcite ($CaCO_3$) and siderite ($FeCO_3$). Although some of the calcite may have been deposited during the peat stage of coal formation, the majority was probably deposited during later periods from water percolating through fractures in the coal bed. The calcite may exist in relatively pure form or may be in combination with clays and/or siderite. The forms most frequently reported are dolomite ($CaCO_3 \cdot MgCO_3$) and ankerite ($2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$).

Silica (quartz SiO_2) may occur in sizable quantities in coal beds with sandstone floors and partings. Other coals are likely to have a very low silica content. It is believed that most of the silica was deposited during the peat stage of coal formation.

In addition to the above, coal may contain a wide variety of other mineral substances of both inherent and extraneous nature, such as calcium, potassium, magnesium, heavy metals and trace elements.

Extraneous materials, as a result of the nature of their deposition, are usually attached to surfaces adjacent to cracks or fractures in the coal and are bound loosely, if at all, to the coal surface. When the coal is mined and processed, these minerals may be distributed throughout the coal. As a result, it is often possible to mechanically remove much of the extraneous mineral matter by washing the

coal. It is logical to assume that any mineral matter contained in coal prepared for slurry pipelines would be thoroughly exposed to the transport water, allowing ample opportunity for any reactions that might occur between coal and water.

Mineral matter containing potentially toxic material is of particular concern from a water quality perspective. Analyses by Chadwick and others (1975) characterized coal from the Rosebud and McKay coal seams in Montana with respect to trace elements. Results of analysis on over 100 samples are summarized in Tables 1, 2, and 3. As noted in Tables 1 and 2, appreciable quantities of toxic metals were found in the coal. Table 3 indicates medium to high sulfur content. It should be noted that coal from these seams is being actively considered for transport by slurry pipeline.

Since contaminant levels in the samples from the Rosebud and McKay Seams are fairly typical of, and in some cases lower than, contaminant levels in samples from other seams, the values in Tables 1, 2, and 3 indicate that potential for water quality degradation from interaction of water and coal certainly does exist. The likelihood of contamination will, of course, depend upon the solubility of these foreign elements in the water.

The Nature of Water (in the Northern Great Plains)

Although other fluids, such as petroleum or other hydrocarbon fuels, could serve as a transport medium in coal-slurry pipelines, it is probable that water will be used in virtually all instances. Hydrocarbon fuels in quantities sufficient to supply a major pipeline operation is not likely to be available in the northern plains coal field area. The characteristics of the water that will be used for this purpose are an important factor in the interactions between the coal and the carrier medium. The chemical characteristics of water vary widely with geographical locations, and with different sources of water at any given location. Since many of the proposed coal-slurry pipelines originate in the northern Great Plains area, the discussion of transport water quality will be limited to waters typical of this area.

Most of the active coal mining in the northern Great Plains is centered in the Powder River Basin in Wyoming and Montana. A map showing the location of the basin is given in Figure 3. Potential sources of water for slurry transport include surface water from local streams; surface water transported into the area from major streams in Montana, Wyoming, and South Dakota; and ground water. Municipal and industrial wastewaters have been suggested as sources of transport water (Buck, 1977); however, the quantity of these waters in the vicinity of the coal mines may be insufficient for even one such operation.

Surface waters in the area are generally of good quality, although of limited availability. It is likely that any surface water available for coal transportation would have to come from impoundments that store runoff during spring snowmelt because the base flow is committed to prior rights in most all instances. Although somewhat turbid and alkaline in nature, this water can be expected to be of good chemical quality.

Ground water, the other potential source of slurry water, is more abundant in the area. The principal aquifer is the Madison formation which underlies much of northern Wyoming, southeastern Montana, and northwestern South Dakota. This 160 km wide, 900 km long aquifer underlies approximately 57,000 square km and is composed of numerous water-bearing formations. The aquifer outcrops in the Black Hills of South Dakota on the east, the Laramie Mountains to the south, and the Bighorn and Pryor Mountains on the west. Recharge from precipitation and snowmelt is extensive, an estimated 185 cubic km per year (Interstate Commerce Commission, 1974). A typical cross section of the aquifer is shown in Figure 3.

TABLE 1. COAL TRACE ELEMENT ANALYSIS: AVERAGE

Element	Analyses in parts per million (ppm) of whole coal, moisturefree basis Rosebud Seam (49 holes)	McKay Seam (26 holes)
Antimony	0.61	0.46
Arsenic	6.02	6.13
Beryllium	0.44	0.45
Cadmium	0.129	0.139
Chromium	5.37	5.30
Copper	12.5	14.6
Fluorine	51.0	19.0
Germanium	2.64	3.98
Lead	8.8	6.4
Manganese	66.1	22.4
Mercury	0.20	0.22
Nickel	37.3	26.5
Selenium	1.29	0.73
Zinc	49.6	15.8

TABLE 2. COAL TRACE ELEMENT ANALYSIS: RANGE

Element	Analyses in parts per million (ppm) of whole coal, moisturefree basis, of 100 samples. Maximum	Minimum
Antimony	2.55	<0.07
Arsenic	21.30	0.68
Beryllium	1.91	0.11
Cadmium	1.510	0.021
Chromium	31.20	<0.40
Copper	40.3	4.6
Fluorine	173.0	4.0
Germanium	16.35	<0.10
Lead	94.0	1.3
Manganese	404.5	6.7
Mercury	0.61	0.08
Nickel	163.5	1.6
Selenium	5.62	<0.07
Zinc	361.0	<1.7

TABLE 3. VERTICAL DISTRIBUTION OF SULFUR IN MCKAY COAL SEAM

Location	%Sulfur (dry basis)
Top one foot of seam	2.22
Intermediate interval (1-7')	1.66
Bottom one foot of seam	3.51

Tables 1-3 from Chadwick, 1975

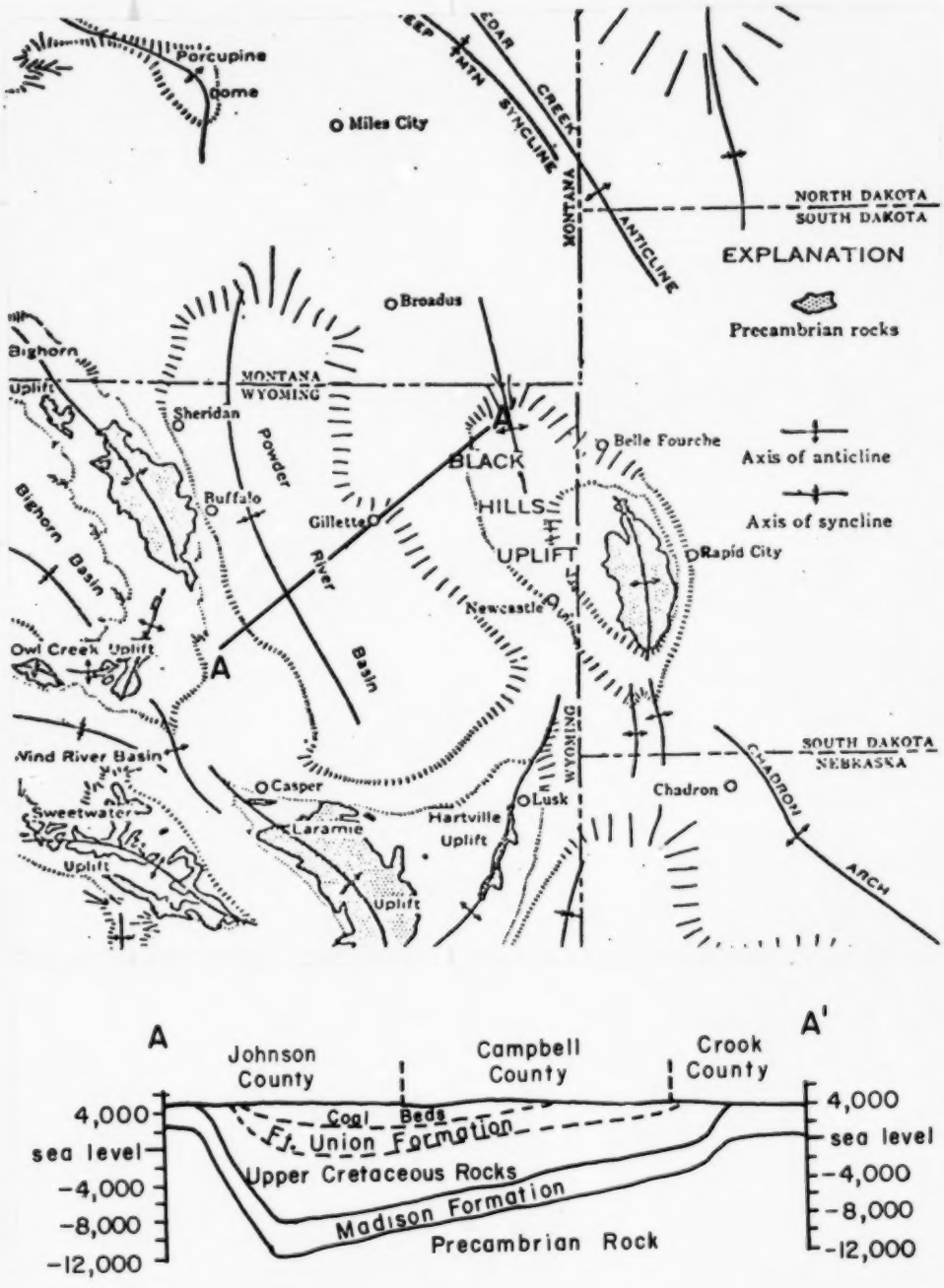

Figure 3. Powder River Basin and Madison Aquifer

The Madison is a deep aquifer except for areas near the outcrop. Parts of the aquifer are 5 km deep. The deeper parts of the aquifer are currently untapped because of drilling expense. Some wells draw water from the shallow parts, particularly along the eastern outcrop, but use is minimal. Thickness of the Madison Aquifer ranges from around 60 m near the south end to around 600 m in the northeast portion (Miller, 1976). The aquifer is mostly fractured rock and has a good hydraulic conductivity. An important feature of the aquifer is that much of it is artesian with a piezometric surface of up to three hundred m above land surface in some areas (U.S. Congress, House, 1975).

The quality of water in the Madison Aquifer ranges from excellent near the recharge areas to extremely poor in the lower reaches of the aquifer. With respect to total dissolved solids (TDS), water in the Madison formation ranges from around 200 mg/l near the recharge areas to as high as 200,000 mg/l in the lower formations (Hopkins, 1976). The U.S.G.S. classification of water with regards to TDS is as follows (Hopkins, 1976):

Classification	TDS
Fresh	< 1000
Slightly saline	1000-3000
Moderately saline	3000-10,000
Very saline	10,000-35,000
Brine	> 35,000

Thus, water in the Madison Formation ranges through the entire classification system. Although there are no active plans to tap the lower part of the aquifer, it has been widely suggested as a source of slurry water because it is (1) too deep to be economically obtainable for municipal or agricultural use, and (2) too saline for most uses even if it were available.

The Nature of Coal-Water Interactions

In a pure molecular state, most of the mineral elements attached to coal are insoluble. However, when combined with other elements in ionic form, most of these contaminants are water soluble to some extent. Appendix A lists the solubility for chloride and oxygen compounds of the elements given earlier in Tables 1 and 2.

If some of the soluble compounds in Appendix A exist as extraneous matter in coal, leaching is likely to occur. In addition, some of these soluble oxides may be formed through exposure to oxygen in the air during mining and grinding operations and/or due to dissolved oxygen in the slurry water. Contact with chlorides in the coal or in transport water could result in some metallic chlorides being formed, especially if large concentrations of chlorides were encountered.

Since little information is available on the form in which these elements appear naturally in coal, one can only speculate on their probable impact on coal-slurry water quality. For example, O'Donnell and Sprunk (1942) reported that significant amounts of lead sulfide (PbS) exist as extraneous matter in coal. Since PbS has a solubility of 86 mg/l at 18°C, it is possible that pumping pulverized coal through a high pressure pipeline could cause some leaching of lead (Peavy and others, 1978).

Alkalinity (the sum of the carbonate, bicarbonate, and hydroxide ions in water) serves as a buffer that resists changes in pH. When water has no buffering capacity, pH can fluctuate widely in the presence of very small amounts of either acids or bases. Well-buffered water, on the other hand, allows for only slight fluctuations in pH, even when relatively large amounts of bases or acids are added to the water. According to a study by Moore (1979), alkalinity concentrations in slurry water under aerobic conditions were reduced as residence time increased. In these

tests, alkalinity did not ever drop to zero. Because of wide variations in coal impurities, there will likely be wide variations in the amount of alkalinity that will leach from the coal. Moore speculates that a simultaneous neutralization of alkalinity in the slurry media and leaching of alkalinity source in the coal can be expected over long slurry runs. However, when the Southern Utah State Water Laboratory (as reported in Anderson and others, 1978) conducted an alkalinity analysis of water from the Black Mesa pipeline, a considerable increase in alkalinity, from that of the source water was recorded.

Hardness (divalent metal cations present in water) of slurry wastewater may be significant enough to require dilution and/or softening of waters which are to be used in heat exchange equipment. Without dilution and/or softening, heat exchange rates are likely to be reduced due to the precipitation of calcium carbonate on the heat exchange surfaces. Moore's study (1979) noted that calcium and total hardness concentrations in the slurry wastewater may be substantial. Godwin and Monahan (1979) report calcium concentration of 553 mg/l resulting from a 50/50 mixture of subbituminous coal and distilled water after a contact time of one day.

Sodium concentrations in Moore's study were only moderately high, with chloride and nitrate concentrations both relatively low. Fluoride concentrations were a function of both coal quality and slurry media water quality.

Analysis for metals by Godwin and Monahan (1979) were made on samples from a 50/50 mixture of subbituminous coal and distilled water after a one day contact period. A portion of their results is shown in Table 4.

The Southern Utah State Water Lab reported increases of an order of magnitude or more in several parameters including TDS, sulfate, sodium, lead, electrical conductivity, turbidity, and copper. Decreases of at least an order of magnitude were noted in both nitrate and zinc (Office of Technology Assessment, 1978). Aside from studies by Moore (1979), Anderson and others (1978), Godwin and Monahan (1979), and the Southern Utah Water Lab (as reported in Office of Technology Assessment, 1978), little data exists about the interaction of coal and distilled, tap, or well water.

The above discussion has primarily involved reports of contamination of fresh water by elements in the coal. As previously mentioned, essentially all of the proposed slurry pipelines will originate in semi-arid regions, where freshwater is a scarce and highly valued resource. To avoid depletion of this resource several alternatives have been proposed, two of which include wastewater effluent and brackish or saline water from deep aquifers.

Anderson and others (1978) and Moore (1979) both analyzed municipal wastewater and coal interactions. However, this writer feels that sufficient quantities of wastewater effluent are not likely to be available for transportation of coal from areas of sparsely populated coal mining regions in the Northwest. Therefore, no discussion of the interaction of wastewater and coal will be undertaken here.

Use of brackish or saline water as a transport medium appears to be an attractive possibility for transport of Northern Plains coal. The characteristics of the Madison aquifer which lies beneath the coal-fields has already been discussed. Although water near the outcrop of this aquifer is of good quality, competition for this more accessible, more usable water will be vigorous. Its use as a transport water in slurry lines is likely to receive low priority. However, no use is currently being made of the saline water in the deeper part of the aquifer.

Use of saline water raises two distinct possibilities: (1) the contamination of the water by metallic chlorides (the very large concentration of chloride in the water is well beyond that needed for chemical combination) and (2) contamination of the coal through adsorption of the elements in the water. The former case would result in problems already discussed and the latter would result in larger quantities of uncombustables (such as fly ash), and also in possible corrosion of power plant equipment. Even if no significant interaction should occur, saline water of this quality is unsuitable for most uses at the pipeline terminus and will not meet standards for discharge into freshwater bodies.

Some data on saline water as a transport medium is available as a result of the study by Anderson and others (1978). In that study, the pH of anaerobic saline solutions decreased as a result of coal contact, as did the alkalinity. However, since the final pH of the water was only slightly below 7, the pH *per se* would not rule out successful reuse of the recovered slurry water. Since the sulfate increased to an extent not totally explainable by solution of sulfate salts, Anderson's report raises the possibility that some sulfur oxidation and sulfuric acid formation may have occurred.

Hardness increased when saline water was the transport medium, probably because of solution of calcium, magnesium, and other hardness minerals from the coal. Sodium and chloride both decreased in the saline slurry. TDS equivalent (total filterable residue) decreased, possibly because of precipitation of saturated species (Anderson and others, 1978).

In addition to the inorganic material discussed previously, it is possible that organic compounds may also result from extended water and coal interaction. Preliminary work at Montana State University (Jennings, 1979) indicates that dissolved organic carbon results from coal and water contact, the amount depending upon several factors including pH, size of coal particles and carbonate precipitation. According to Moore (1979) biochemical oxygen demand (BOD) of slurry water ranges as high as 156 mg/l, an indication that some organic compounds do exist.

A study of saline water use in energy development by Israelsen and others (1980) included an investigation of saline water as a transport medium. Coal from four mines in central and southeastern Utah were slurried with water in which TDS varied from 2,200 mg/l to 13,200 mg/l. It was found that orthophosphate and nitrate nitrogen were consistently adsorbed by the coal while silica, boron, strontium, organic carbon and chloride were consistently leached from the coal by the water. Other parameters, magnesium and carbonate, were sometimes leached while fluoride, aluminum, potassium and sodium were sometimes adsorbed onto the coal and sometimes leached into the water.

Obviously, the data available to date do not give a complete picture of the interactions that may occur between coal and water when water is used as a slurry transport medium. There is at this moment a dearth of published information concerning water and coal interaction under conditions such as those that occur in coal-slurry pipelines. While there is considerable information about mine drainage and runoff from coal stockpiles indicating that significant water quality degradation can be caused by contacting water and coal, such degradation occurs in the presence of oxygen. More research is needed to indicate what interactions occur under anaerobic conditions such as those encountered in a pipeline.

Considering the fact that a tremendous surface area is created by pulverizing coal to the size used in slurry pipelines and that the coal and water are violently agitated for many days under high pressure with some increase in temperature likely, there is cause for concern regarding contamination of transport water in the coal-slurry process. It was in reponse to this concern that the Montana State University project was initiated to investigate the nature and extent of any contamination of water resulting from its use in a coal-slurry pipeline.

SECTION 5

PROJECT DESCRIPTION

The objective of the Montana State University research project was to determine the nature and amount of substances that can be expected to remain in slurry transport water after the water and coal have been separated. Of particular interest were those substances that would be considered pollutants if discharged to the environment. The project was initially planned to utilize both pilot-scale facilities and laboratory models to duplicate as closely as possible actual pipeline conditions. Run lengths of 12 days were selected to model detention times in prototype pipelines currently under consideration.

This section of the report describes in detail the equipment used and the materials and methodology employed for modeling slurry system conditions, and the techniques used for obtaining and analyzing slurry samples.

EQUIPMENT

Pipeline

The research pipeline facilities at Montana State University consist of a 732 m loop of 22 cm diameter American Petroleum Institute (API) steel pipe flanged together in 18.3 m lengths. The pipeline is connected to a 30 × 25 cm centrifugal pump powered by a 114 kilowatt D.C. motor. Direct current is supplied to the motor by rectifying and filtering 440 volt A.C. current. Rheostat controls allow variable pumping rates. Instrumentation is available for automatic flow control through feedback from pump discharge and suction pressure, flow rates, and motor speed, or the system can be operated with manual controls. Flow measurement is provided by a 20 cm magnetic flowmeter. The meter is connected to a graphical recorder to provide records of flow rates. Manometers are provided on the suction and discharge sides of the pump as well as at 3 locations in the pipeline.

Three runs were attempted using the pilot pipeline facilities, each ending due to mechanical failure after about one day of operation. The pump is equipped with double mechanical shaft seals which are seated just behind the impeller. Contact surface of the seals are graphite rings and must be cooled by circulating water through the seal box. A delicate balance must be maintained between pressure in the seal box and pressure on the pumpage side of the seal. Under ordinary pumping conditions, a slightly greater pressure is maintained in the seal box and slight leakage through the seals prevent the fluid being pumped from entering the seal.

When pumping a coal slurry, the prevention of leakage back through the seals is essential since the coal granules are very abrasive and will quickly destroy the seal rings. Conversely, significant leakage through the seals to keep the coal slurry washed back cannot be tolerated either. Extraneous water from the seal box dilutes the slurry and destroys the closed loop system. The addition of fresh water changes the environment for coal-water interaction.

While the above dilemma appears straightforward and logical in hindsight, its discovery was empirical and deduced from many frustrating events. As far as the researchers were able to determine, other experiments have not been conducted in which similar closed loop systems were used to pump a coal-slurry. Pump manufacturer's literature makes no reference to the necessity of a forward leakage, and the researchers were assured that the system, "properly operated," should work. After three unsuccessful attempts, it was determined that approximately 2.0 liters per minute of leakage through the seals and into the pumpage was necessary to prevent destruction of seal parts and subsequent complete mechanical failure.

In order to maintain the desired velocity in the pipeline, the pumpage rate was approximately 3,000 liters per minute. A leakage of only 2 liters per minute represents a very small fraction of the total flow. In prototype pipelines delivering slurries from one point to another, this leakage is insignificant, a fact emphasized by pump manufacturers. However, leakage of 2 liters per minute would result in a total leakage of 2,880 liters per day. Since the capacity of the system being used was approximately 17.25 m^3, a leakage of 2 liters per minute would result in a 200% dilution of the slurry over the 12-day period for which pumping was planned.

Other problems were also encountered in attempting to use the pipeline facilities. A little over 8 tons of coal were required to obtain a 50/50 mixture of water and coal sufficient to fill a 460 m section of the pipeline. It took approximately 6 hours to prepare this quantity of the mixture. Since the mixing system was open to the atmosphere, an aerobic system atypical of coal-slurry operations exists for a considerable period of time.

Considering all the problems involved, an agreement was reached with the granting agency to abandon the pilot pipeline and complete the project using only a bench scale reactor. Since aerobic conditions existed during much of the coal-water contact time, data generated during the three aborted runs is of questionable utility and is not reported in this document.

Bench Scale Reactor

Several factors were considered in the design of the bench scale reactor. These included volume, turbulence, maintenance of an anaerobic environment, and ease of sampling.

As previously stated, twelve day runs were selected to bracket long pipeline detention times. Sampling at selected intervals over this period was included to establish rates of interactions. To avoid inconsistencies due to variability in initial coal quality, the reactor was sized to contain at least enough slurry to provide all the samples required over one 12-day run.

Coal-slurry pipelines are designed for turbulent flow in order to keep coal particles in suspension. Thus, turbulent conditions should be maintained in the reactor. Since most chemical reactions are expected to occur at water-coal interfaces, sufficient turbulence to keep the coal particles suspended, thus maximizing exposed surfaces, was deemed essential.

The quantity of oxygen available for oxidative reactions in coal slurry pipelines is limited to the dissolved oxygen initially present when the coal is slurried. Anaerobic conditions are expected to develop quickly and a reducing environment maintained throughout the remaining length of the pipe. Provisions for excluding air from the reactor was therefore considered necessary. Provisions for sampling without opening the reactor to the atmosphere were considered essential.

To meet the above objectives, the bench scale reactor was built as follows. A 102 cm length of 38 cm diameter PVC pipe was obtained and the ends were closed with 2.5 cm aluminum plates. Eight tie rods along the outside of the reactor held the system together. The volume of the reactor

was approximately 116 liters (ℓ). Location of the sampling port at the center restricted the volume available for samples to slightly less than one half this amount. Turbulence was provided by rotating the reactor about its longitudinal axis. The reactor was placed on steel bars mounted at each end in pillow blocks. Torque was applied directly to the reactor by a sprocket and chain arrangement powered by an electrical motor. Four baffles, made from 5 cm wide strips of lucite, were glued to the inside of the reactor running the full longitudinal length. These baffles prevented the coal from packing into a lump and sliding around the bottom of the reactor as it turned.

A 6.5 mm sampling port was drilled and tapped into the center of one end plate and a valve was installed for sampling. A port was also provided for the injection of nitrogen gas into the reactor to maintain an anaerobic system. A positive pressure of approximately 69 kPa was maintained at all times and was also quite useful in expelling the sample. A 5 cm plug was drilled and threaded into the side of the PVC pipe for loading water. Figures 4 and 5 provide views of both ends of the reactor.

MATERIALS

Materials used for the slurry were coal from the Western Energy Mine at Colstrip, Montana, and dechlorinated tap water from the Bozeman, Montana, water system. The coal came from the Rosebud Seam and was shipped in run-of-the-mine condition to the Mineral Research Center at Butte, Montana, for grinding. The coal was ground by roller-crusher and hammer mill to the size shown in Table 4. After grinding, the coal was placed in plastic bags in 55 gallon drums, sealed tightly to prevent air entrainment and subsequent oxidation, and trucked to Bozeman.

The specific gravity (dry) of six random samples of the coal averaged 1.33 with only a slight variance. The moisture content ranged from 16 to 25 percent with an average value of 21 percent. Whether the variance in moisture can be attributed to actual differences as mined or to handling after mining could not be determined.

In all, four runs (B1, B2, B3, B4) were made using the reactor and the coal described above. These runs included both fresh water and saline water as a transport medium. Additionally oxygen-scavening and friction-reducing chemicals were added to one fresh water and to one salt water run. Chemicals used for this purpose were sodium hexametaphosphate (oxygen scavenger) and a product

TABLE 4. GRAIN SIZE ANALYSIS OF GROUND COAL
(U.S. Bureau of Standards)

Sieve no.	Mesh size (mm)	Percent by weight retained on sieve	Cumulative percent retained
16	1.19	0.88	0.88
20	0.840	10.24	11.12
40	0.420	36.45	47.57
50	0.297	15.53	63.10
70	0.210	10.57	73.67
100	0.149	9.36	83.03
140	0.105	5.51	88.54
200	0.074	4.30	92.84
325	0.045	4.96	97.80
400	0.037	0.88	98.68
pan	--	1.32	100.00

Figure 4.
Coal-slurry
Reactor,
Sampling End.

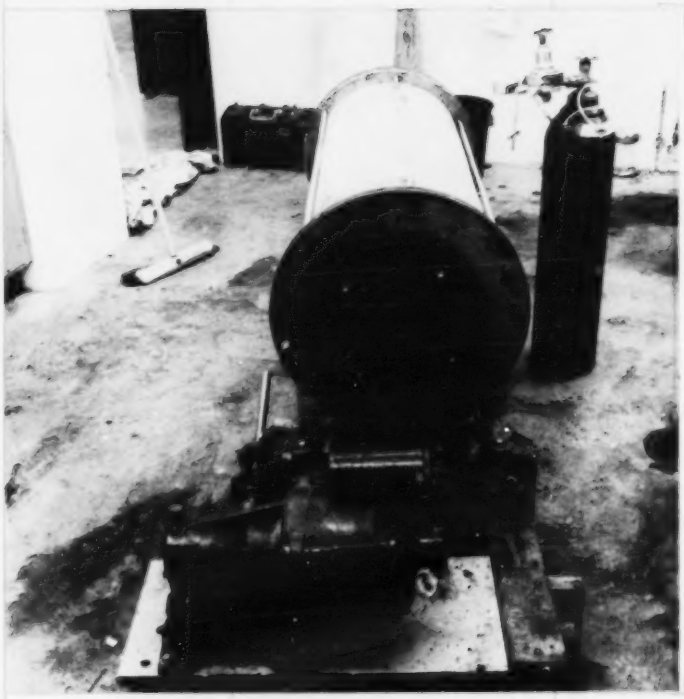

Figure 5.
Coal-slurry
Reactor,
Drive End.

product called 3 + III/SA produced by FMC Corporation (friction reducer). The latter material, a phosphate-sodium-alkali mixture that acts as a dispersant, prevents particles from agglomerating into larger masses so that the slurry is less viscous. Tests by Faddick* indicate a considerable reduction in head loss due to friction by the addition of 0.9 kg of this chemical per ton of coal (0.1 percent by weight).

METHODOLOGY

Run B1

In run B1, coal and fresh City of Bozeman tap water only were used. The mix-water was first aerated to remove chlorine. A predetermined quantity of coal, 62 kg was placed in the reactor and the end plates bolted tight. The reactor was then placed on the roller and sufficient water (63 ℓ) was added to completely fill the reactor. The reactor was turned at a rate of 10 revolutions per minute, and a sample was taken as soon as thorough mixing had occurred (approximately 5 min). Nitrogen gas was injected under pressure to expel the sample and to prevent air entrainment. Throughout all runs, a positive pressure of about 69 kPa of nitrogen was maintained in the system. All samples were taken while the reactor was rotating in order to remove a well mixed sample, and thus not thicken the remaining slurry. Approximately 3 ℓ of slurry was removed for each sample.

Run B2

The water and coal used in run B2 were from the same sources as the water and coal used in run B1. Sodium hexametaphosphate equivalent to the oxygen content of the water (0.418 g) and 64 g of the FMC friction reducer were added in dry form to the coal. Water was then added to form the slurry. The remainder of the procedure was the same as in run B1.

Run B3

Run B3 used coal from the same batch and saline water as the transport medium. The saline water was prepared by aerating 70 ℓ of Bozeman tapwater, to which had been added the following amounts of materials.

Material	Amount (g)	Material/Water Ratio (mg/l)
Na_2SO_4	248.5	3,550
$MgCl_2$	16.8	240
$CaCl_2$	98.0	1,400
NaCl	1528.0	21,830

This water would approximate the composition of water withdrawn from some parts of the Madison aquifer. Ionic concentration of this water is approximately as follows:

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*Dr. Robert Faddick, Professor of Civil Engineering, Colorado School of Mines, Golden, Colorado. Personal communication.

Cation	Concentration		Anion	Concentration	
	mg/l	meq/l		mg/l	meq/l
Ca^{++}	500	25	$SO_4^{=}$	2,400	50
Mg^{++}	61	5	Cl^{-}	14,400	400
Na^{+}	9600	420			
Totals		450			450

The container of water was mixed overnight and inspected to make sure that no precipitate remained. The required amount of this solution was used as the liquid medium in run B3.

Run B4

Run B4 consisted of coal, saline water, the oxygen scavenger, and the friction reducer. The procedure for composing and mixing the saline water was the same as in run B3, and quantities of sodium hexametaphosphate and FMC friction reducer were the same as in run B2.

SAMPLING AND ANALYSIS

Sampling Schedule

The sampling schedule was designed to determine the rate at which reactions occurred as well as the extent to which the reactions occurred. To provide background data, samples of the water used as a transport medium were taken prior to the addition of the coal (mix water). Next, a sample was taken immediately after mixing of the slurry was completed (0 hour). Thereafter, samples were taken at increasing intervals of time. Sampling intervals for each of the runs are listed below. In addition, analyses of the solid coal were made before slurrying and after the maximum contact time.

Mix Water	
0 hour (immediately after mixing)	2 days
6 hours	4 days
12 hours	8 days
24 hours	12 days

Sample Analysis

Testing parameters were selected to be representative of materials that would be considered pollutants if discharged in quantity to surface waters. Tests selected to be run on a routine basis were as follows:

Physical parameters

- pH (run immediately after sampling)
- specific conductance (μmhos cm^{-1} @ 25°C)

Mineral parameters

- alkalinity
- chloride
- nitrate
- phosphate
- sulfate

Metals		
sodium	chromium	mercury
manganese	copper	nickel
arsenic	lead	zinc
Other parameters		
turbidity	oxygen conditions	Chemical Oxygen Demand (COD)
Organic parameters		
Dissolved Organic Carbon (DOC)	phenols	High Performance Liquid Chromatographic (HPLC) Profiles

Samples were processed immediately after they were taken. For all parameters except the organics, aliquots of the samples were placed in 150 mℓ centrifuge cups and centrifuged at about 2000 rpm's (810 × G) for approximately 20 minutes. Although the distinguishable particles were packed into the bottom, the liquid on top was still quite colored, in dark brown hues. The liquid was decanted and then filtered through a 0.45 μ plastic filter under vacuum.

For heavy metal analysis, one hundred milliliter aliquots were separated, placed in glass jars and acidified with nitric acid. All containers with processed samples were filled completely full and capped tightly to minimize contact with air.

Analysis for pH was performed using a Corning Model 12 Research pH meter. This test was run immediately after sampling and before sample processing. Conductivity was measured using a Lab-line Lectro mHO-meter (Model MC-1, Mark IV). Chemical parameter analyses were conducted according to procedures outlined in Methods for Chemical Analysis of Water and Wastes, EPA, 1976, or equivalent. Nitrates were run with specific ion probes and an Orion Research Model 801 A digital ionanalyzer. Sulfates were run by turbidimeter method. Heavy metals were analyzed by atomic absorption.

Samples for analysis of dissolved organic carbon and HPLC were handled in the following manner. Approximately 100 mℓ of sample (or 1 ℓ, if HPLC was to be performed) were drawn from the slurry vessel. The samples were centrifuged at 8K for ~20 minutes using a Beckmann ultracentrifuge. The water was decanted and filtered through a 0.25μ silver metal membrane (Selas Corporation) using a Gelman pressure filtering apparatus.

For analysis of dissolved organic carbon, triplicate 5 mℓ aliquots of sample were transferred to precombusted glass ampoules (Oceanography International) containing 0.25 gm potassium persulfate. A Hamilton "Gas-Tite" syringe was used for the transfer. Six percent H_3PO_4 (0.25 mℓ) was added to each ampoule. Each sample was purged for 8 minutes with oxygen that had been passed over a catalyst at 500°C and sealed immediately. This procedure was carried out on an Oceanography International ampoule sealing unit. Sealed ampoules were autoclaved at 100 kPa for about 15 hours (overnight). Samples were then analyzed using a Total Carbon Analyzer (Oceanography International).

Lab work involving the separation of hydrophobic acids from organic solutes proceeded as follows. Concentrated HCl was added to the prepared sample to bring the pH to 2*. The sample was allowed to stand overnight and then was filtered through No. 4 ashless paper. A 15 × 250 mm

*Precipitate contained "humic acid," filtrate the "fulvic acid."

column was packed with XAD-2 resin until half full, then finished with XAD-8. The column was supported so that the XAD-8 was on the bottom. One liter of doubly-distilled water was pumped through from bottom to top. One liter of sample was then pumped onto the bottom of the column at a rate of 5 mℓ/min.[†] The column was disconnected and inverted. The pump and lines were flushed with 0.1 N NaOH before reconnecting the column. NaOH (100 mℓ, 0.1 N) was pumped onto the bottom of the column (XAD-2). The highly colored portion of the effluent (usually the first 10-20 mℓs to be collected after clearing the column of water) contained the hydrophobic acids. The column was then cleaned by flushing with 500 mℓ of methanol followed by 500 mℓ of doubly distilled water. The column was then inverted to original configuration and flushed with an additional 500 mℓ doubly distilled water.

In preparation for methylation of hydrophobic acids, equal amounts of hydrophobic acids and a mixture of water, methanol, and 1,2-dimethoxyethane (6:7:7) were heated and stirred in a 3-neck flask. The pH was adjusted to 11 with NaOH. The flask was fitted with a condenser, thermometer, pH electrode, and a nitrogen purge tube adjusted to purge at a slow rate. The flask was heated to 60°C and dimethylsulfate (200 μℓ) was added. After the pH fell below 5, it was readjusted to 11. This cycling was repeated until pH would no longer drop to 5, or until the reaction had proceeded for 72 hours. The reaction mixture was then brought to pH 7 with 1 N NaOH. This solution was evaporated on a Buchi "Rotovapor" and the methylated product was redissoved in 15 mℓ doubly distilled water and filtered through a 0.45 μ millipore-type HA filter.

A Waters Associates High Pressure Liquid Chromatography system equipped with a 254 nm UV detector, a C_{18} μ Bondapak column and a solvent programmer was used for further analysis of soluble organics. A 25 μℓ sample of methylated hydrophobic acids in doubly distilled water was injected into the system. A linear solvent gradient of 0 percent to 100 percent acetronitrile in water was run for 15 min at a flow rate of 1 mℓ/min.

Phenol analysis of samples was carried out according to the Folin-Ciocalteu method. Into an acid-cleaned test tube, 2 mℓ of sample, 7 mℓ of two percent Na_2CO_3, and 0.5 mℓ of 1 M Folin and Ciocalteu's reagent (Sigma Chemical Co.) were placed. The tube was covered, shaken, and placed in a 21°C water bath for 30 minutes. Blanks were prepared by the same procedure with doubly distilled water in place of sample. Absorbance at 720 nm was measured by means of Varian model 634 UV-Vis spectrometer.

In addition to liquid samples, analyses were also performed on samples of the solid coal. Analysis of the solid coal was made by digesting the coal in appropriate acids. Acid bombs were used for metals with subsequent measurement by atomic adsorption spectroscopy (Varian carbon rod atomizer). Chlorides were acid bombed and measured by wet chemical techniques. Fluoride was acid digested and measured with a specific ion probe and sulfur was digested in a barium solution and measured by atomic emission.

[†]The effluent contained the most polar component.

SECTION 6

RESULTS AND DISCUSSION

The data are presented in tabular and graphic form in the following pages of this report. A discussion of physical parameters (pH and electrical conductivity), mineral compounds (alkalinity, chlorides, nitrates, sulfates, phosphates), metals (sodium, manganese, arsenic chromium, copper, lead, mercury, nickel, and zinc), other parameters (turbidity, oxygen conditions, and COD), and organic parameters (DOC, phenols, and HPLC profiles) accompanies presentation of the data.

PHYSICAL PARAMETERS

pH

The pH of a water is a measure of the molar concentration of hydrogen ions in solution. Mathematically, the pH is the negative log of hydrogen ion concentration (or the log of the reciprocal of the hydrogen ion concentration). The pH of the slurry system is important for several reasons. The solubility of metals is pH dependent, with low pH values resulting in soluble species and high pH values resulting in precipitation of metallic hydroxides. Changes in pH of the slurry system can result from chemical reactions that release hydrogen or hydroxyl ions into the water. An important consideration in coal-slurry systems would be the reaction of sulfur, water, and oxygen to form sulfuric acid and lower the pH of the slurry.

The pH of the slurry samples was determined immediately after sampling. The pH data is listed in Table 5 and is shown graphically in Figure 6. A pH drop of approximately one to two units was observed immediately upon mixing of the water and coal. While some variance was noted in the pH during the course of the 12 day run, the change was slight and showed no trends. Apparently, the reaction responsible for the pH changes occurred quickly and was not reversed during the course of the run. In this particular experiment, the pH change *per se* should not constitute a problem in reuse of water from coal-slurry pipelines. However, it would be noted that these data cannot be extrapolated to coals of different characteristics, particularly coals of different sulfur content.

Specific (Electrical) Conductance

Because the ability of water to conduct electricity is a function of its ionic strength, a measurement of the electrical conductance of a sample yields an indirect measurement of the total dissolved solids in the water. Electrical conductance is the inverse of electrical resistance; therefore, it can be measured as the reciprocal of resistance (ohms) and is expressed as mhos. Since the resistivity of pure water is quite high, the conductivity is a small number. Thus, the common practice is to express conductivity as 10^{-6} mhos, or micromhos. As an example, distilled water might have a conductivity of 0.5 to 2 μmhos/cm, while an industrial water with a high TDS might measure 10,000 μmhos/cm.

TABLE 5 pH (units)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	7.8	6.6	6.0	5.9	5.9	5.8	6.0	6.3	6.2
B2	7.6	6.1	6.1	6.1	--	6.3	6.0	6.4	6.1
B3	8.3	6.2	6.0	5.9	6.2	6.2	6.3	6.3	6.3
B4	8.2	6.2	6.0	5.6	5.9	5.9	5.9	6.0	6.1

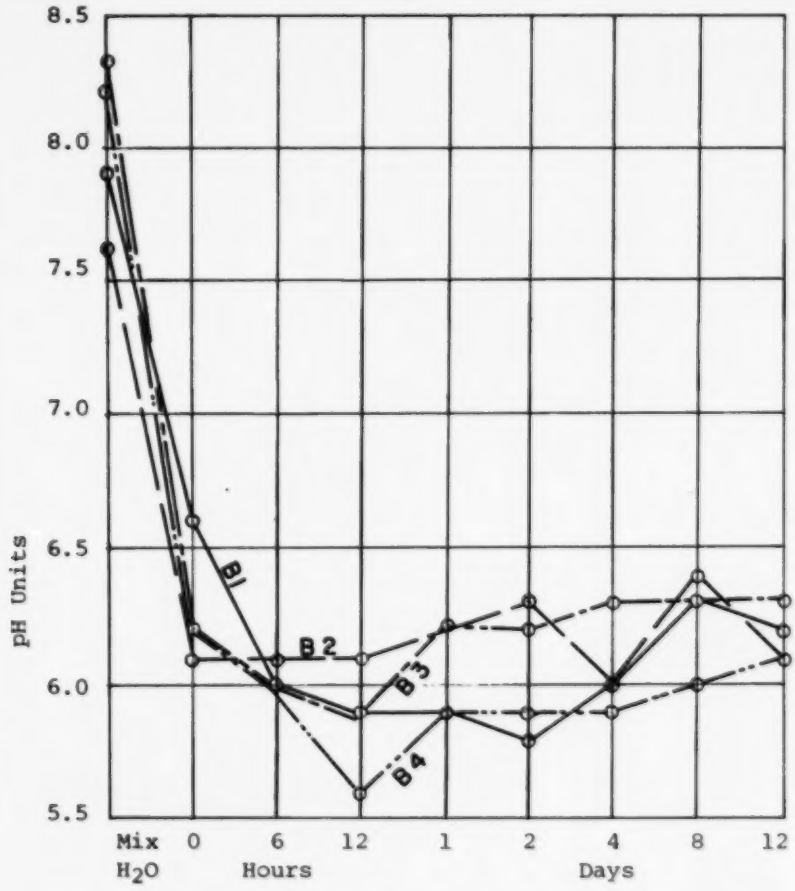

Figure 6. pH vs. Time

The breadth of the electrical field, the temperature of the water, and the electromobility of the ions also affect the electrical conductance. The standard procedure is to control these variables by measuring the conductance in a one cubic centimeter field and at a temperature of 25°C. A conversion factor, which depends upon the chemical nature of the solution, is used to convert from micromhos/cm to ppm of TDS. The conversion factor to mg/ℓ usually varies from 0.55 to 0.9 depending upon the composition of the solution. In this study, a multiple of 0.65 was used to convert electrical conductivity to TDS.

The electrical conductivity of the slurry systems is presented in Table 6 and is shown graphically in Figure 7. These results indicate that the TDS of fresh water is increased by contact with the coal while saline water loses some TDS when contacted with the coal. Whether this loss is a result of adsorption of the minerals to the surface of the coal, or of chemical combination with minerals in the coal and subsequent precipitation, has not been determined.

MINERAL PARAMETERS

Alkalinity

Alkalinity is defined as the quantity of negative ions which will react to neutralize hydrogen ions. Alkalinity is thus a measure of a water's ability to neutralize acids. The principal components of alkalinity in most water are bicarbonate (HCO_3^-), carbonate ($CO_3^=$) and hydroxide (OH^-) ions. Alkalinity is usually expressed as mg/ℓ of $CaCO_3$, or as milliequivalents per liter. As noted earlier, the practical significance of alkalinity is that it is a measure of the buffering capacity of the water. Water with a high alkalinity will resist pH changes when either an acid or a base is added. The pH will fluctuate rapidly in low alkalinity water with the addition of only small quantities of acids or bases. Water with extremely high alkalinity is caustic and cannot be used for many purposes.

The alkalinity of a coal-slurry system is important primarily from the buffering capacity standpoint. If sufficient alkalinity is present, pH reduction that is a result of the reaction of sulfur compounds with water will be avoided.

Alkalinity data are presented in Table 7 and are shown graphically in Figure 8. In runs 1 and 3, the alkalinity was seen to drop initially and then rise substantially. The rise was continuing at the end of 12 day runs. Thus, alkaline substances are being leached from the coal. The source of the alkalinity is believed to be the calcium oxide that are ubiquitious to western coals.

Runs in which the chemical additives were used behaved in a slightly different manner. Alkalinity of the initial mixture was increased because of the alkali base of the friction retardant. Apparently, the chemical reacted with the ions in saline water in run B4 because initial alkalinity concentrations were lower. Decrease in the alkalinity thereafter may have been because of the adsorption of the chemical onto the coal particles or because of ion exchange (calcium in the coal for sodium in the chemicals) and subsequent precipitation of calcium carbonate. Adsorption could be expected because the purpose of the chemical is to adsorb to and sequester the coal particles. Ion exchange and precipitation would also be expected because of the thermodynamics of the reactions. (See discussion of ion exchange potential in section on sulfate.)

Alkalinity of the magnitude shown in runs 1 and 3 could be troublesome in some uses at the pipe terminus. Scaling could be a problem, particularly if the water becomes a part of recycled cooling water. Of particular concern is the fact that all runs show rising values at the 12 day sample. This indicates that equilibrium conditions have not been reached and that longer retention times might result in even greater concentrations.

TABLE 6 ELECTRICAL CONDUCTIVITY
(micro mhos per centimeter @ 25°C)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	197	1190	1190	1220	1430	1510	1680	1420	1940
B2	152	1600	2150	2190	2120	2140	2180	2290	2300
B3	52,400	48,200	49,700	46,300	49,200	49,700	47,200	51,200	49,100
B4	44,000	41,400	42,400	42,900	42,700	42,900	44,000	43,800	44,100

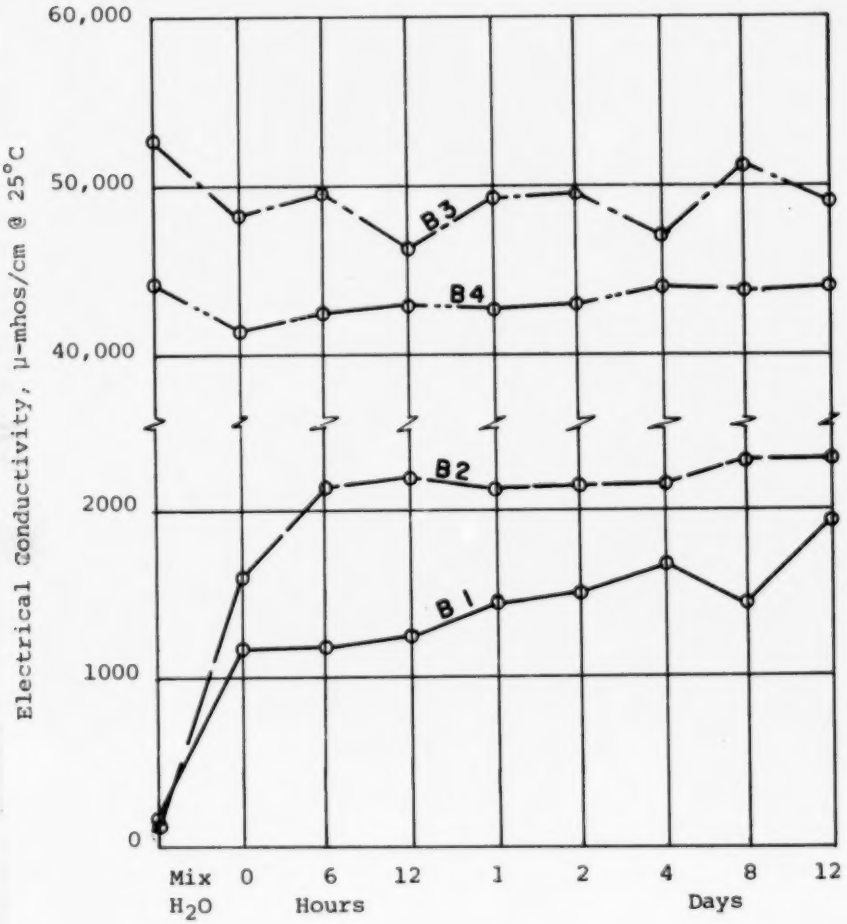

Figure 7. Electrical Conductivity vs. Time

TABLE 7 ALKALINITY as $CaCO_3$(mg/1)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	97	32	52	75	102	179	290	471	558
B2	78	257	87	70	54	56	100	170	236
B3	96	20	29	34	54	110	183	317	385
B4	95	112	66	61	44	44	74	138	190

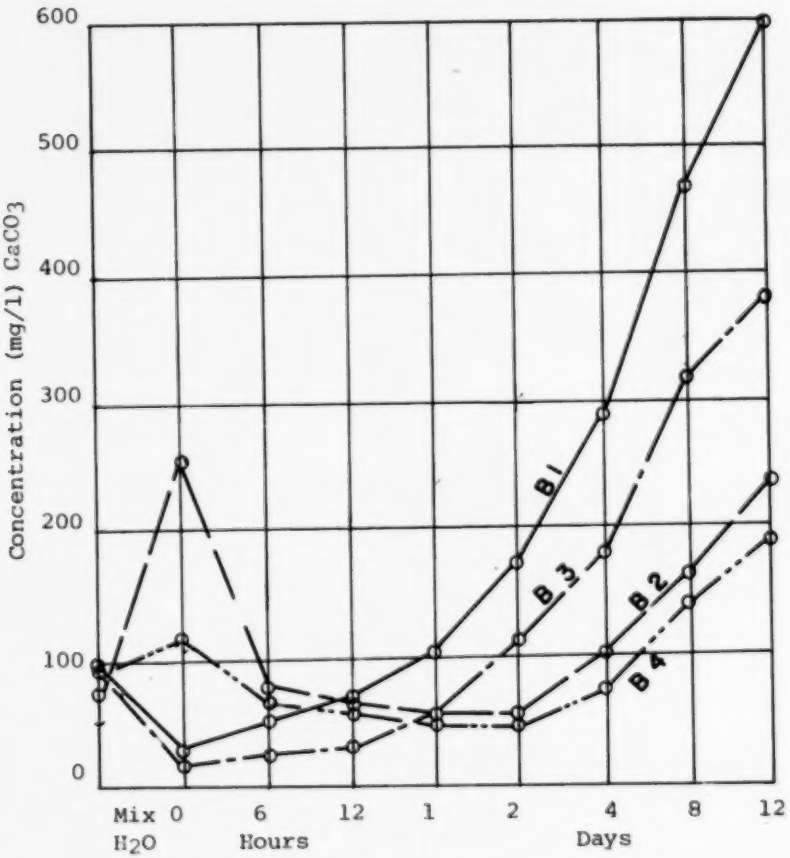

Figure 8. Alkalinity vs. Time

Chlorides

Chloride is a ubiquitous constituent of natural waters. Concentrations may range from a few parts per million to several thousand parts per million depending on the geological formations with which the water has been in contact, or on its previous use. Limiting values depend on proposed uses. In most cases, a few hundred parts per million can be tolerated.

In slurry pipeline systems, the most important characteristic of chloride would be its corrosive nature. Chlorides have been reported to have an adverse effect on metals associated with water handling systems at concentrations as low as 45 mg/ℓ (McKee and Wolf, 1963). Higher concentrations could be expected to accelerate corrosion rates.

Chloride data for this experiment are given in Table 8 and are shown graphically in Figure 9. Mix water for the fresh water runs contained very low concentrations of chlorides and showed little change after contact with the coal. Saline water runs had very high initial concentrations and showed decreases after mixing with the coal. The decrease (up to 1500 mg/ℓ) in run B3 may be because of adsorption to the coal surface, or of combination with elements in the coal and subsequent precipitation. In either event, the chloride would probably accompany the coal during the separation process.

Nitrates

Nitrate is the oxidized form of nitrogen. It may originate as inorganic nitrogen from the atmosphere, or as organic nitrogen from decomposition of plant or animal tissue. In most cases, nitrate is formed by microbial oxidation of organic nitrogenous materials. Nitrate is a plant nutrient that promotes growth of most species of aquatic plants and could thus lead to biological fouling of heat exchangers or other cooling tower components or to problems of accelerated biological growth in receiving streams.

The nitrogen content of coals is probably quite low. Parks and O'Donnell (1957) found concentrations of nitrogen ranging from 1.2 to 2.1 percent by weight in subbituminous and bituminous coals. It has been postulated that the nitrogen is associated with aromatic compounds such as pyrroles and carbazoles in the coal (Anderson and others, 1978). Although nitrates are sometimes found in ash from the combustion process, it is likely that oxidation occurred during the burning process and that the nitrogen was not in nitrate form in the coal (Anderson and others, 1978).

Although some opportunity for microbial oxidation of the nitrogen in the coal might exist during the grinding and slurrying operation, the depletion of oxygen in the pipeline would arrest the biological nitrification process. Additionally, aromatic structures are difficult to degrade biologically. Thus, significant concentration of nitrates should not be expected in coal-slurry systems unless the nitrate was initially present in the transport water.

Nitrate data from the experiments are presented in Table 9 and are shown graphically in Figure 10. Data are graphed only for the fresh water runs because it is believed that the data for the saline water runs are in error. As previously mentioned, nitrate tests were run by the specific ion electrode method. Ionic concentrations of the magnitude encountered in the saline water will produce erroneous readings on the high side. This was obviously the case because the mix water showed excessive concentrations of nitrate after the salts had been added. The freshwater data indicate that nitrates should not be a problem in coal-slurry transport water.

TABLE 8 CHLORIDE (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	4.12	4.6	4.6	4.9	5.5	4.7	5.0	4.4	4.3
B2	4.2	8.0	5.7	5.7	5.5	5.7	5.3	5.3	6.3
B3*	1.52	1.44	1.38	1.38	1.34	1.36	1.44	1.37	1.36
B4*	1.29	1.29	1.26	1.25	1.21	1.23	1.19	1.24	1.26

* mg/l x 10^{-4}

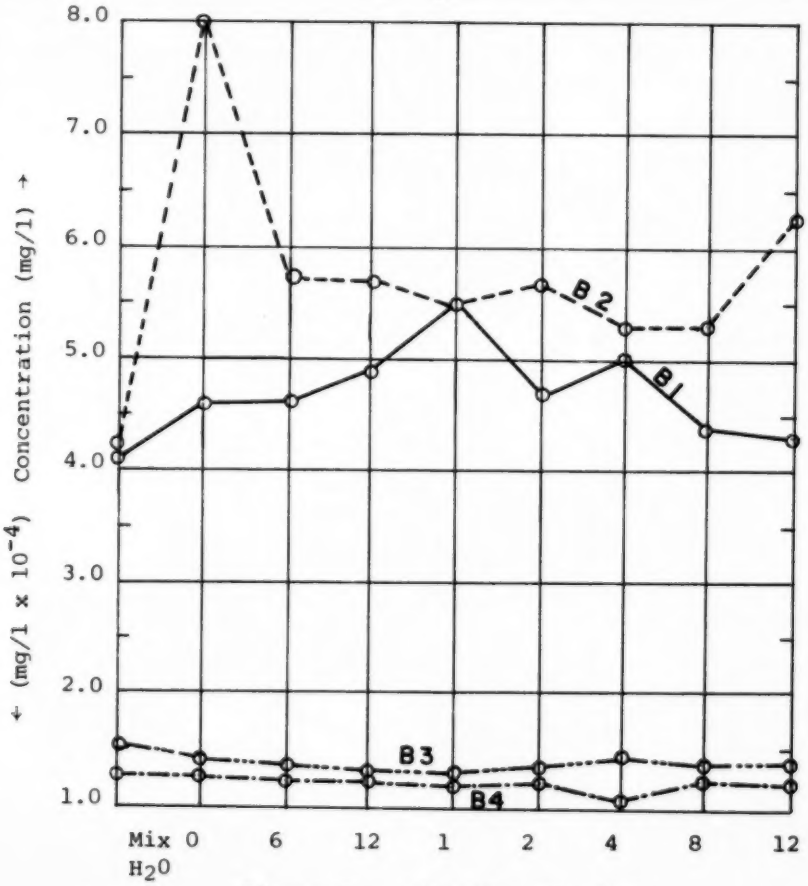

Figure 9. Chloride vs. Time

TABLE 9 NITRATE (NO_3) NITROGEN (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.4	0.3	0.3	0.5	0.5	0.4	0.5	0.6	0.2
B2	0.1	0.3	0.3	0.2	0.2	< 0.2	< 0.2	< 0.2	< 0.2

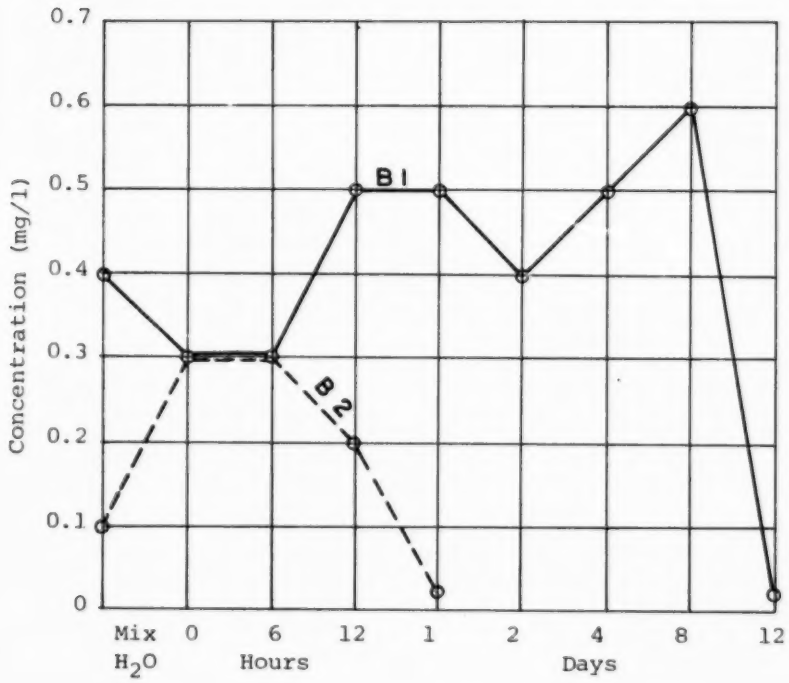

Figure 10. Nitrate (NO_3) Nitrogen vs. Time

Sulfates

Sulfates may exist naturally in water that has contacted mineral deposits such as gypsum. Additionally, sulfates may result from the biological oxidation of sulfides and sulfites. In excess concentrations, sulfates impart an unpleasant taste to water and may have a laxative effect on the consumer. Plant growth may be affected adversely at lower concentrations. McKee and Wolf (1963) suggest that concentrations below 500 mg/ℓ be permitted in water intended for consumption by humans and livestock, and that concentrations below 250 mg/ℓ be permitted in water intended for irrigation.

In coal-slurry systems, sulfate from oxidized sulfur compounds in the coal may become dissolved in the transport water. Biological oxidation of pyrites can also result in dissolved sulfates. Thus, fresh water used as a carrier medium could acquire a substantial concentration of sulfates.

Sulfate data are presented in Table 10 and shown graphically in Figure 11. The fresh water run (B1) shows an appreciable increase in sulfate concentrations up to the six-hour sample. The reaction then appears to level off, indicating that equilibrium conditions have been approached. However, other factors besides chemical equilibrium may be affecting the reaction. The availability of free oxygen necessary for biologically mediated oxidation of sulfur to sulfates may have become exhausted at this point (see section on oxygen conditions). No aerobic tests were run to determine whether or not sulfates would continue to be formed if oxygen were present because pipeline conditions are assumed to be anaerobic.

Sulfate data from the other runs are a little more difficult to interpret. Chemical additives for corrosion inhibition and friction reduction appear to increase the sulfate concentration substantially (runs B2 and B4). However, neither material contains sulfur or sulfur compounds. There must, therefore, be some other reason for this occurrence.

One possible explanation would be ion exchange between the chemical additives (or the salt in run B4) and the sulfate compounds in the slurry water. If the compounds formed in the freshwater run were, for example $CaSO_4$, some precipitation may have occurred (only the soluble fractions were measured in the analysis). With additional ions present, perhaps chemical combinations such as $CaCO_3$ occurred, removing part of the calcium from solution and resulting in the formation of another, more soluble sulfate compound (say Na_2SO_4).

Initial concentrations of sulfates in the salt water runs (runs B3 and B4) were high because of the presence of $MnSO_4$ in the water. The reaction in run B4 has already been discussed. Run B3 (salt water, no chemical additives) behaves differently from any of the others. The sulfate concentrations in this run decline slowly but steadily throughout the run. This would indicate chemical combinations resulting in less soluble compounds (possibly $CaSO_4$) and subsequent removal of part of the sulfate either as a precipitate or by adsorption to the coal. This would tend to support the hypothesis that the chemical additives in runs B2 and B4 resulted in the creation of more soluble components of sulfur through ion exchange processes.

In any event, the concentrations of sulfate encountered in this project indicate a potential problem in utilization and discharge of the slurry water at the pipe terminus. Actual problems will depend, of course, on the degree to which the slurry water is diluted prior to use or discharge.

Phosphates

Phosphorus occurs in water almost exclusively as phosphates. The general term phosphates include orthophosphates, condensed phosphates (pyro-, meta-, and polyphosphate) and organic

TABLE 10 SULFATE (mg/1)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	12	700	860	866	866	866	900	900	960
B2	20	815	1375	1375	1900	1525	1550	1500	1500
B3	2080	2250	2175	2175	2175	2046	1900	1900	1750
B4	2516	2870	3151	3041	2784	3263	3325	3325	3325

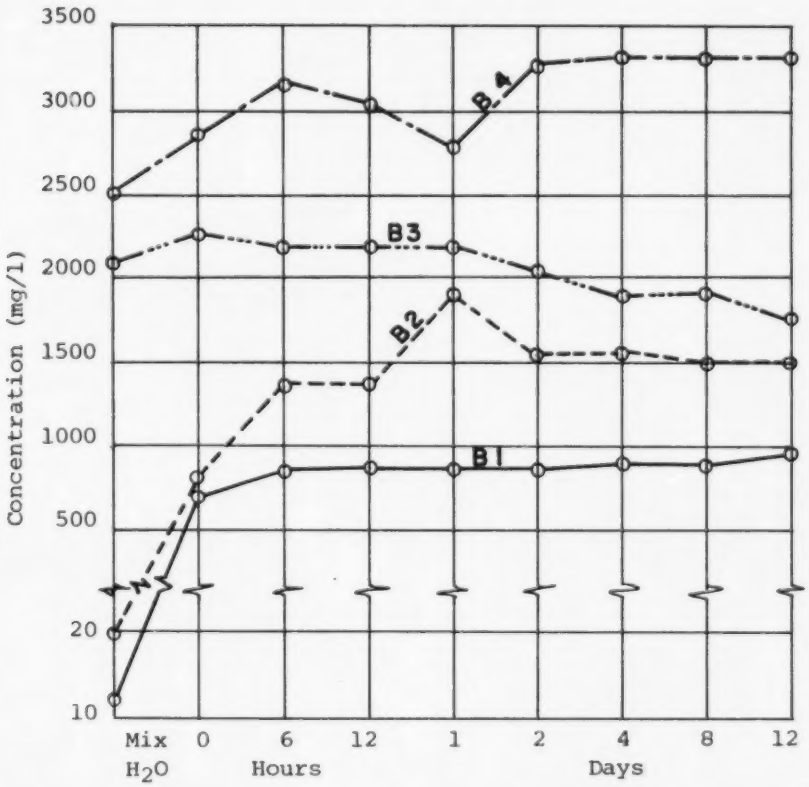

Figure 11. Sulfate vs. Time

phosphates. Generally, orthophosphates are assumed to be the soluble form with condensed phosphates being precipitates. Although this is not completely true, the approximation may be close enough for most work. Soluble organic phosphate is not usually present in most waters in significant concentrations.

Phosphates were measured in the slurry experiments in which friction and corrosion inhibitors were added to the transport water. Phosphates added were in the condensed form, and analyses were performed to determine the fraction that solubilized to orthophosphates. The data is presented in Table 11 and shown graphically in Figure 12.

The results indicate that a large amount of phosphate solubilized initially and that soluble concentrations then decreased. This is expected since phosphate tends to form complexes with metallic cations and metalloids, some of which are only slightly soluble.

Phosphates in the concentrations observed in this experiment could cause difficulty in the reuse or discharge of the separated slurry water. Phosphate is an essential nutrient for plant growth. When other necessary nutrients are already present, excessive concentrations of phosphate unduly accelerate plant growth. This could present a problem with biological fouling of heat exchangers and other cooling tower components if the water is reused in the power plant cooling system. Ultimate discharge of portions of the water could also present problems of accelerated biological growth in receiving streams.

METALS

Sodium

Of the elements in the Earth's crust, sodium ranks sixth in abundance. Sodium is very active chemically and occurs only in compounds in nature. Most sodium salts are extremely soluble in water. Excessive sodium concentrations render water unpalatable for drinking purposes and constitute a health hazard to cardiac and kidney patients. Additionally, high sodium concentrations constitute a hazard to plants and may limit the use of water for irrigation. Sodium is also corrosive to metal surfaces.

Sodium is an element common to most coals. The sodium content of the coal used in this experiment ranged from 0.02 to 0.03 percent. It would be anticipated, therefore, that some interaction of this material with water would occur. Data for sodium are given in Table 12 and shown graphically in Figure 13.

Data for the freshwater runs indicate dissolution of some sodium from the coal (run B1) and a considerable increase from the coal and from the chemicals added in run B2. Concentrations of the range found in run B1 should present no problems. While concentrations of the range shown in run B2 might be restrictive for some uses, such concentrations are not considered excessive.

In the salt water runs (runs B3 and B4) concentrations of sodium in the mix water were quite high and are seen to decrease with time. Because there are no known constituents of the coal with which sodium will form precipitating complexes, it is assumed that the sodium salts were adsorbed onto the surface of the coal and remained there during the separation process. Sodium content of the coal before and after slurrying (see section on changes in coal composition) confirms this. Consequences of sodium adsorption to coal include a greater volume of fly ash produced upon combustion and possible corrosion of furnace elements.

TABLE 11 PHOSPHATE (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
1									
2	0	8.3	80	91	71	49	43	33	27
3									
4	0	63	50	36	26	22	37	32	32

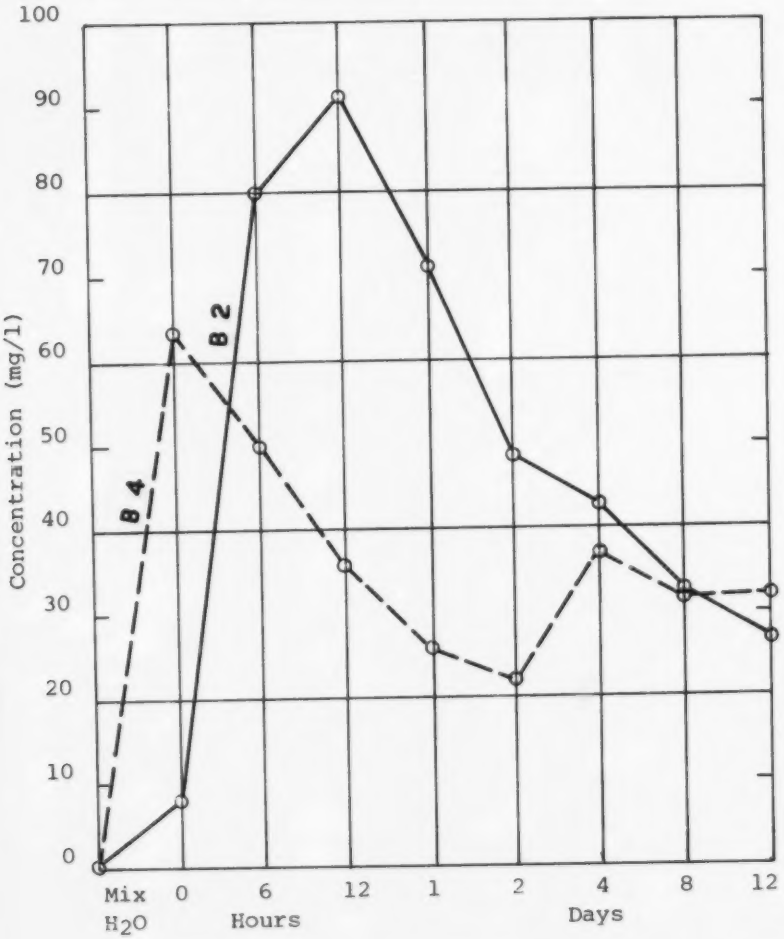

Figure 12. Phosphate vs. Time

TABLE 12 SODIUM (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	3.0	55	65	66	69	71	68	76	79
B2	142	299	248	233	230	231	226	241	248
B3	9080	8390	7360	7520	7080	7450	7240	7200	7300
B4	9250	6955	6280	6090	7040	6100	6005	6150	6123

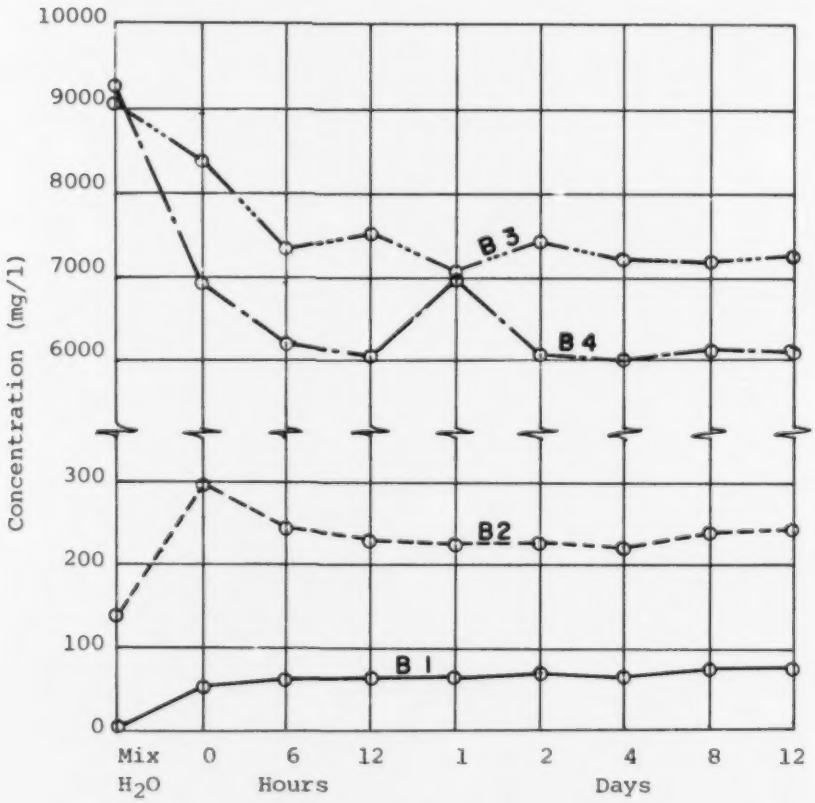

Figure 13. Sodium vs. Time

Manganese

Manganese is not found in pure form in nature but its compounds and ores are common and widespread. Quite frequently manganese compounds and iron compounds occur together. Some forms of manganese (chlorides, nitrates, and sulfates) are highly soluble, while other forms (oxides, carbonates, and hydroxides) are only slightly soluble in water. Thus, reducing environments result in greater solubilities of manganese compounds. Manganese concentration as low as 0.15 mg/ℓ may be aesthetically objectionable and expensive to treat, but it is usually not harmful to health.

As discussed previously, manganese is found in quantity in Northern Plains coal. Concentrations averaged 94 ppm in the coal used for this experiment. Data for soluble species in the transport water are presented in Table 13 and shown graphically in Figure 14.

The data show concentrations of manganese considerably in excess of 0.15 mg/ℓ. The salt water runs show the greatest concentration, probably an indication of the formation of manganese chloride, which is more soluble than other species. Trends indicate a slight increase toward the end of the run, which may be significant if longer pipelines are built and transport time increases.

Concentrations of manganese of the magnitude shown in this experiment would definitely cause turbidity problems. The extent of this problem would depend upon the use to which the water is put and the degree of dilution provided by additional process water or receiving streams. In an oxidizing environment, precipitation of much of the manganese could be expected, which might cause problems in cooling systems.

Toxic Metals

As noted in earlier discussions, several metals that are commonly found in coal are toxic to organisms. Many of these metals are in appreciable amounts in Northern Plains coal. Toxic metals chosen for analysis in this project were arsenic, chromium, copper, lead, mercury, nickel, and zinc.

While all of these metals are practically insoluble in their elemental form, salts or other compounds may be highly soluble. Chromium, copper, lead, mercury, nickel, and zinc are highly soluble when combined with the anions chloride (Cl), nitrate (NO_3), and sulfate (SO_4). These metals are relatively insoluble when combined with carbonates, oxides, and hydroxides. When combined with oxides to form arsenates, arsenic may be quite soluble, while oxides of hexavalent chromium combine with metallic cations to form soluble compounds. Thus, all of these metals are soluble in one form or the other.

Arsenic, chromium, lead, and mercury are highly toxic to humans and other biological species. Additionally, arsenic, lead, and mercury are cumulative toxins. EPA drinking water standards for arsenic, chromium, and lead limit concentrations to 0.05 mg/ℓ and set standards of 0.003 mg/ℓ for mercury. Copper and zinc are toxic in quantities of several parts per million, although taste problems interfere with use before toxicity levels are reached. However, a unique problem exists with these two metals in that they are synergistic in small concentrations when present in solution together. Little information is available on the toxicity of nickel to humans. However, it is known to be toxic to plants in fairly low concentrations (McKee and Wolf, 1963).

Data for toxic metals are shown in Tables 14 through 20 and in Figures 15 through 21.

In general, most of the toxic metals are seen to increase slightly above background concentrations in the mix water. Concentrations of these metals remain quite low, however. It is interesting

TABLE 13 MANGANESE (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	<0.01	0.25	0.34	0.37	0.38	0.45	0.53	0.63	0.66
B2	<0.01	1.52	0.99	0.80	0.64	0.66	0.73	0.77	0.85
B3	0.04	2.46	3.56	3.88	3.88	4.13	4.30	4.41	4.36
B4	0.01	2.61	2.47	3.40	3.40	3.48	3.70	3.78	3.84

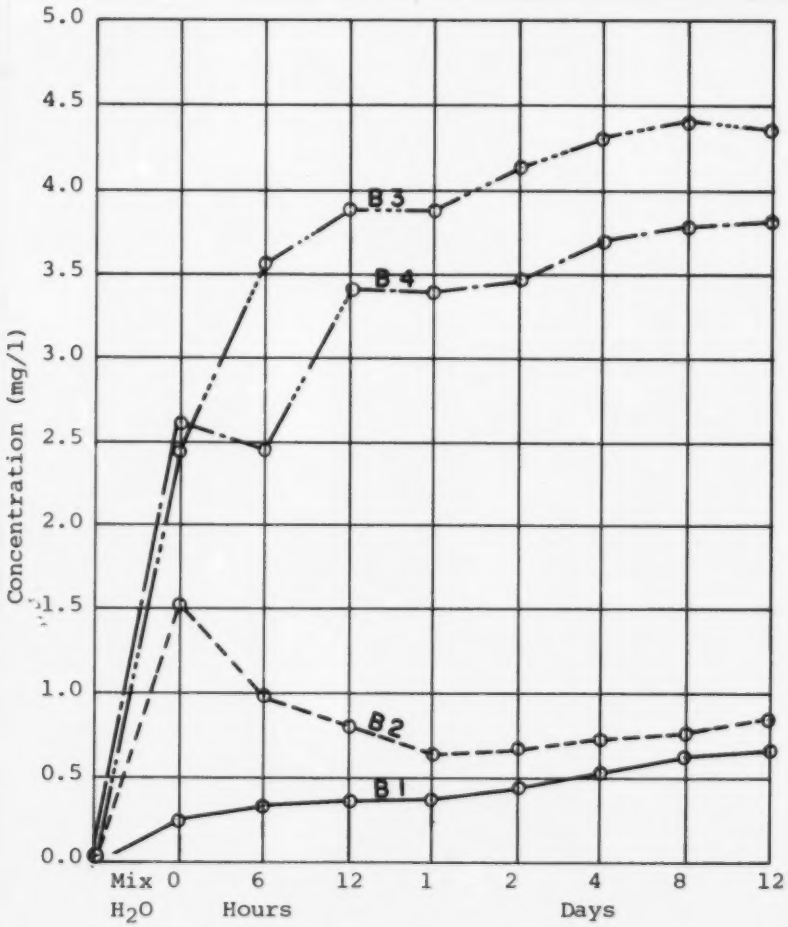

Figure 14. Manganese vs. Time

TABLE 14 ARSENIC (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.011	0.014	0.014	0.014	0.021	0.013	0.018	0.028	0.026
B2	0.014	0.046	0.058	0.084	0.084	0.110	0.112	0.060	0.073
B3	0.012	0.017	0.023	0.020	0.023	0.024	0.024	0.027	0.027
B4	0.006	0.010	0.034	0.049	0.075	0.026	0.011	0.027	0.080

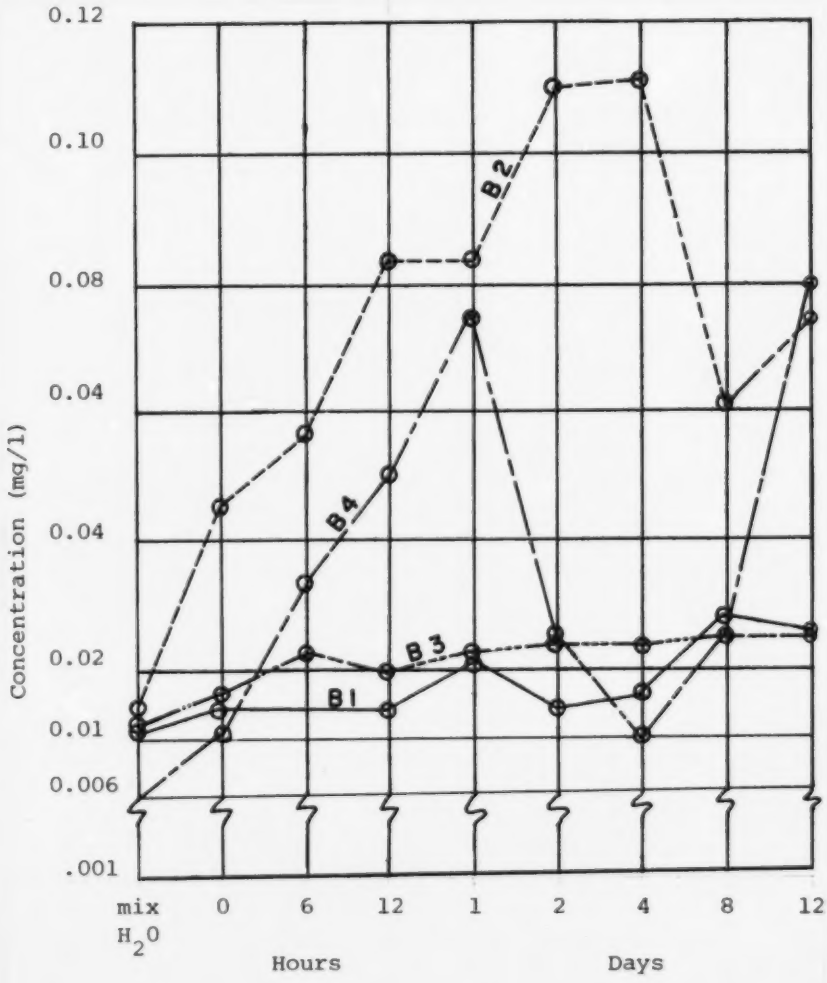

Figure 15. Arsenic vs. Time

TABLE 15 CHROMIUM (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	< 0.0010	0.0010	0.0015	0.0015	0.0010	0.0010	0.0010	0.0010	0.0010
B2	< 0.0010	0.0040	0.0020	0.0040	0.0030	0.0060	0.0060	0.0040	0.088
B3	0.093	0.60	0.072	0.072	0.045	0.067	0.057	0.057	0.067
B4	0.006	0.009	0.005	0.006	0.006	0.006	0.006	0.006	0.007

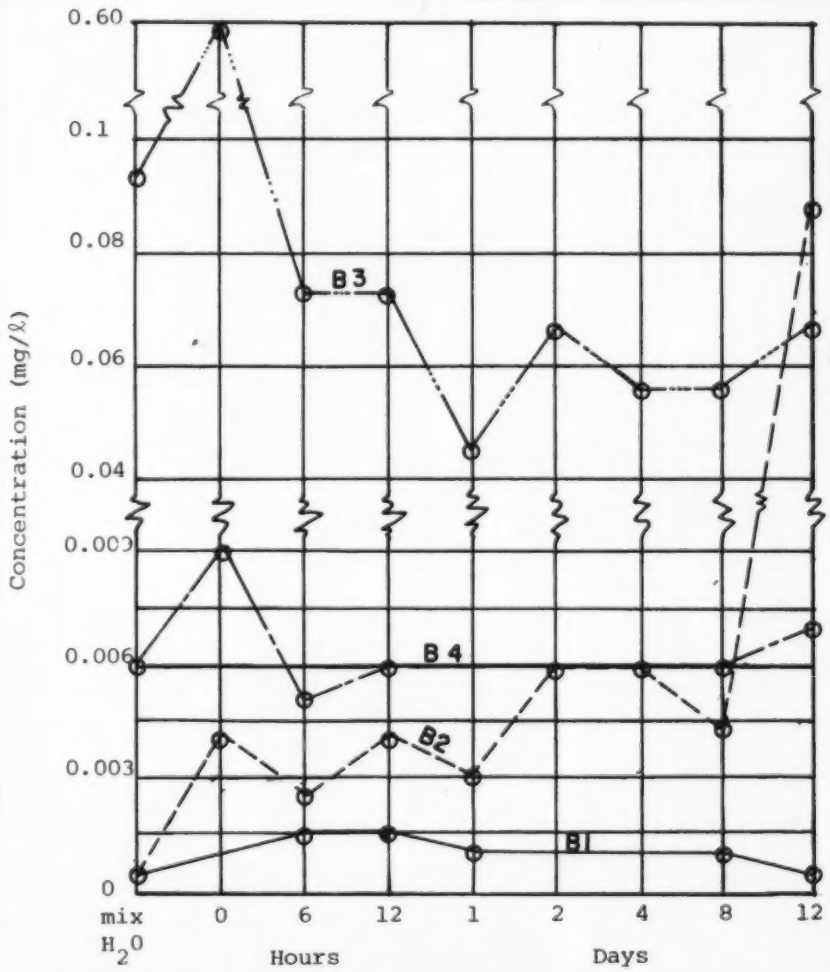

Figure 16. Chromium vs. Time

TABLE 16 COPPER (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.07	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03
B2	0.16	0.05	0.03	0.06	0.05	0.03	0.05	0.04	0.04
B3	0.48	0.09	0.07	0.13	0.07	0.07	0.07	0.07	0.07
B4	0.18	0.07	0.07	0.11	0.11	0.08	0.07	0.07	0.08

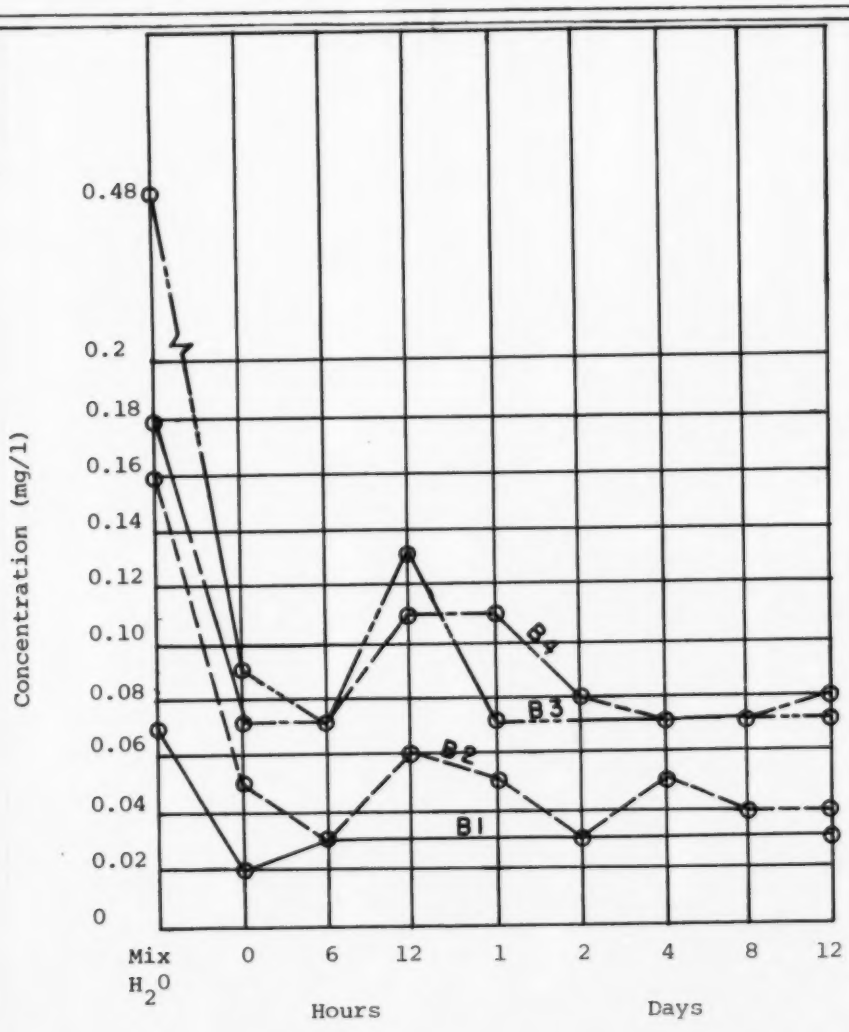

Figure 17. Copper vs. Time

TABLE 17 LEAD (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.006	0.04	0.036	0.035	0.030	0.020	0.033	0.035	0.045
B2	0.006	0.040	0.025	0.045	0.045	0.030	0.050	0.045	0.045
B3	0.038	0.037	0.025	0.022	0.017	0.016	0.020	0.015	0.030
B4	0.020	0.020	0.012	0.016	0.018	0.010	0.007	0.019	0.015

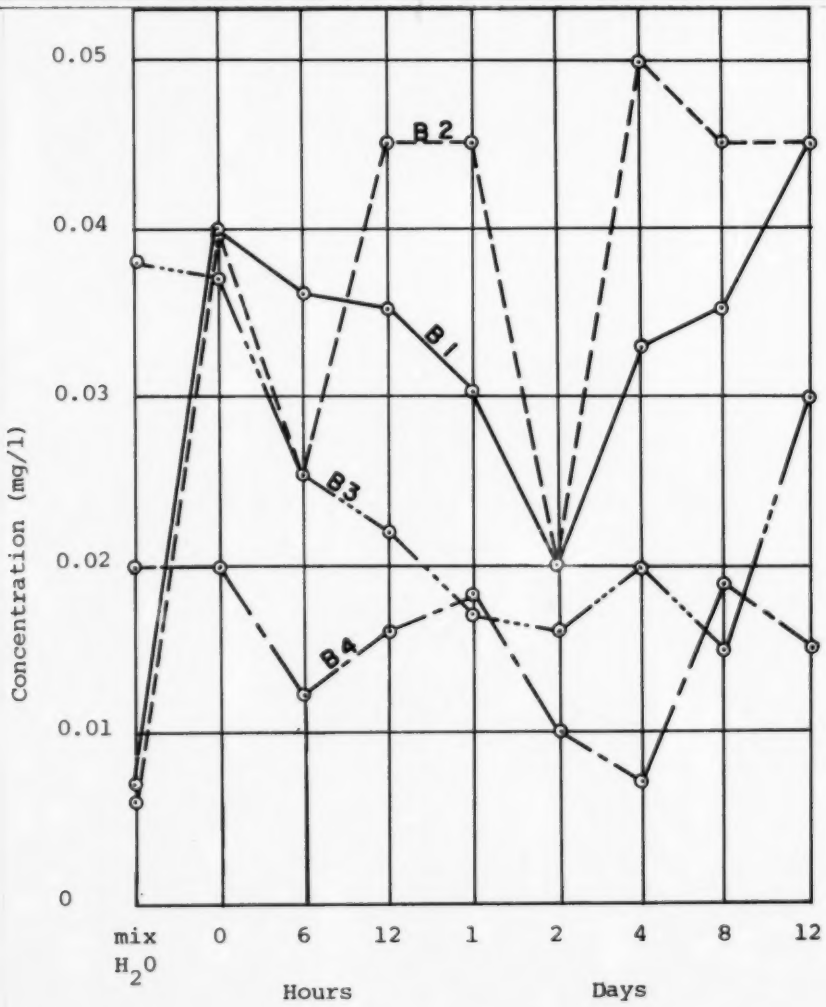

Figure 18. Lead vs. Time

TABLE 18 MERCURY (mg/1 x 10^3 [parts per billion])

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.74	7.60	0.30	0.28	0.37	0.12	0.22	0.52	0.30
B2	0.24	0.73	0.33	0.48	0.24	0.45	0.16	0.34	0.43
B3	0.78	0.75	0.66	0.58	0.31	0.25	0.34	0.22	0.29
B4	1.54	0.45	0.03	0.05	0.04	0.01	0.19	0.08	0.93

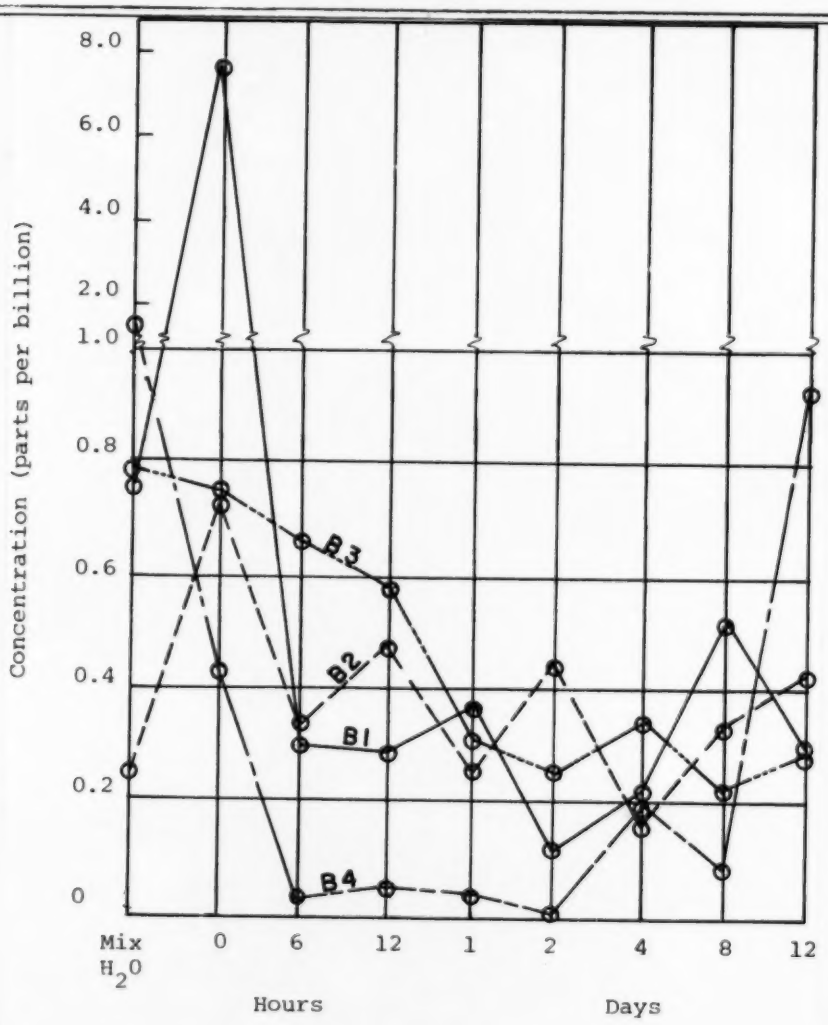

Figure 19. Mercury vs. Time

TABLE 19 NICKEL (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
B2	0.005	0.03	0.005	0.025	0.005	0.005	0.015	0.005	0.005
B3	0.010	0.010	0.010	0.010	0.010	0.010	<0.010	<0.010	<0.010
B4	0.01	0.007	0.012	0.035	0.012	0.017	0.007	0.011	0.013

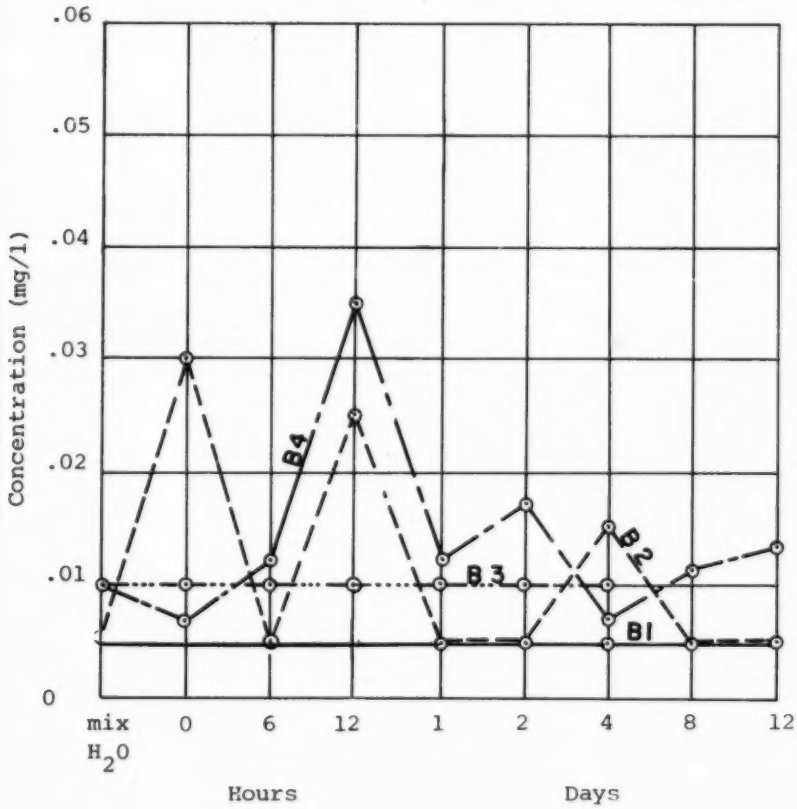

Figure 20. Nickel vs Time

TABLE 20 ZINC (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	0.02	0.06	0.04	0.05	0.05	0.03	0.05	0.04	0.04
B2	0.04	0.18	0.07	0.08	0.07	0.09	0.06	0.09	0.09
B3	0.10	0.25	0.64	1.02	0.70	0.81	1.20	1.85	0.74
B4	0.55	0.66	0.37	0.55	0.73	0.59	0.96	0.43	0.24

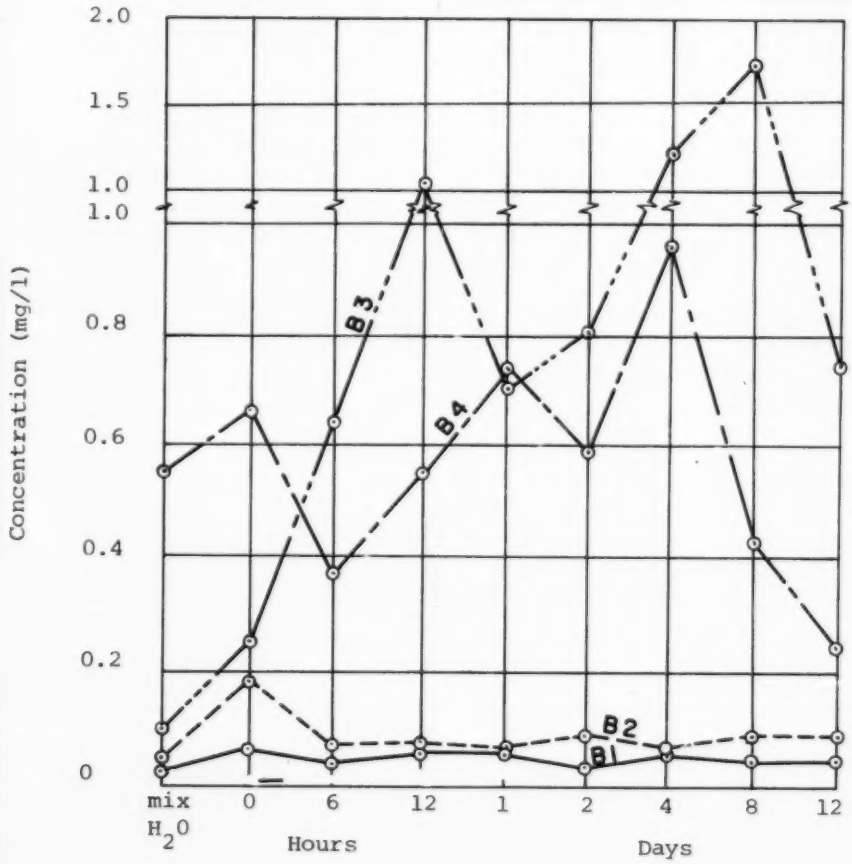

Figure 21. Zinc vs. Time

to note that while arsenic and nickel are more soluble in the presence of the chemical additives, chromium, copper, and zinc were more soluble in the salt water, and lead appears more soluble in the fresh water. At the concentration noted, however, toxic metals do not appear to be a significant source of pollution in slurry transport water with respect to EPA drinking waterstandards.

It should be noted at this point that the pH of the system strongly influences the solubilities of these metals. At alkaline pH values, the metals tend to form compounds with hydroxides and carbonates and to precipitate out, but at lower pH values, solublecompounds are formed. The relationship between pH and solubility of several of the metals is shown graphically in Figure 22. As an example, at a pH of 6, lead is soluble to 10^{-6} moles (0.21 mg/ℓ), and at a pH of 4, it is soluble to 10^{-2} moles (2072 mg/ℓ). Thus, the solubility of these metals would probably increase significantly if the pH of the slurry systems were lowered by two to three units. As noted earlier, coals of higher sulfur content might well lower the pH farther than did the coal used in the MSU experiments.

OTHER PARAMETERS

Turbidity

Turbidity in water results from suspended particulate matter which scatters light and produces a "cloudy" appearance. Turbidity is, therefore, an indirect measure of suspended solids. Quantitatively, turbidity cannot be correlated to suspended solids because the size and number of particles have a greater effect on turbidity than does total mass of particles.

The level at which turbidity becomes objectionable depends upon the proposed use of the water. For example, high turbidity levels in water to be discharged into receiving streams may be objectionable because turbidity in surface water bodies decreases light penetration and increases heat absorption. Both of these factors may alter biological and chemical reactions occurring in water. Turbid water is less pleasing aesthetically, and turbidity-producing particles may serve as adsorption sites and transport vehicles for bacteria.

Turbidity in coal-slurry systems is difficult to measure and must be interpreted with care. Turbidity was not routinely run on all samples during this experiment for reasons that should be obvious in the following discussion.

Turbidity is measured by either light scatter (nephelometry) or by light absorption. Most turbidimeters used in water quality analysis today are nephelometers. A beam of light of calibrated intensity is directed through a sample of standard size and the light that is reflected at an angle of 90° is measured by a photometer. The result is expressed as a number of turbidity units referenced to a standard.

Because black coal particles absorb rather than reflect light, any turbidity analysis must be on an absorption basis. The results obtained in a light scatter reading are misleading because thicker slurry water suspensions produce smaller, in stead of greater, readings on a nephelometer.

The slurry becomes black immediately upon mixing the coal and water. Turbidity measurements of raw slurries cannot be made directly, but by dilution with turbidity-free distilled water absorption readings were taken; these readings showed that slurries of the nature used in these experiments had a turbidity in excess of 45,000 JTUs.

Unless one is considering the effects of a slurry spill on a stream or lake, the turbidity of the slurry itself is not an important parameter. What is important is the turbidity remaining in the water

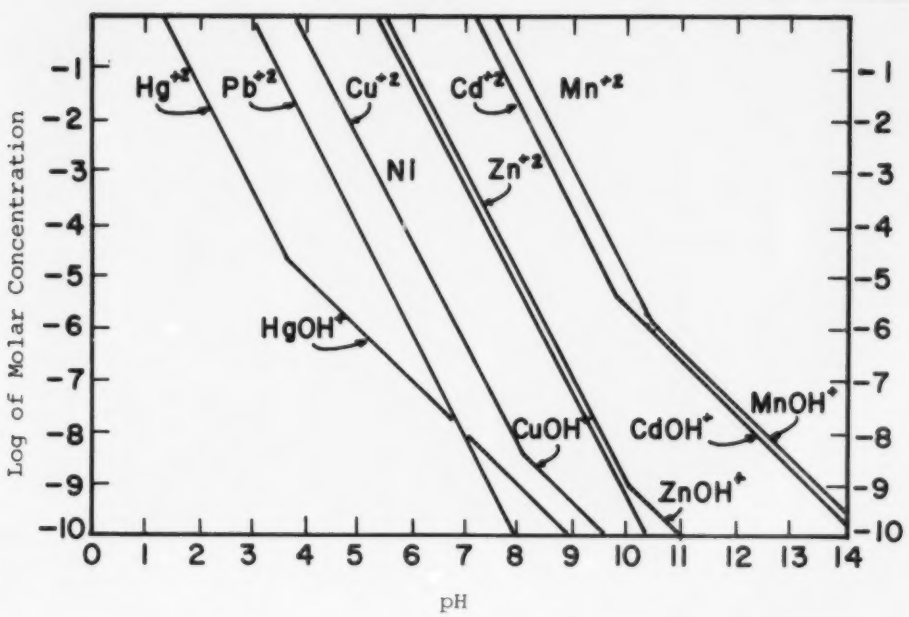

Figure 22. Solubility of Metals vs. pH

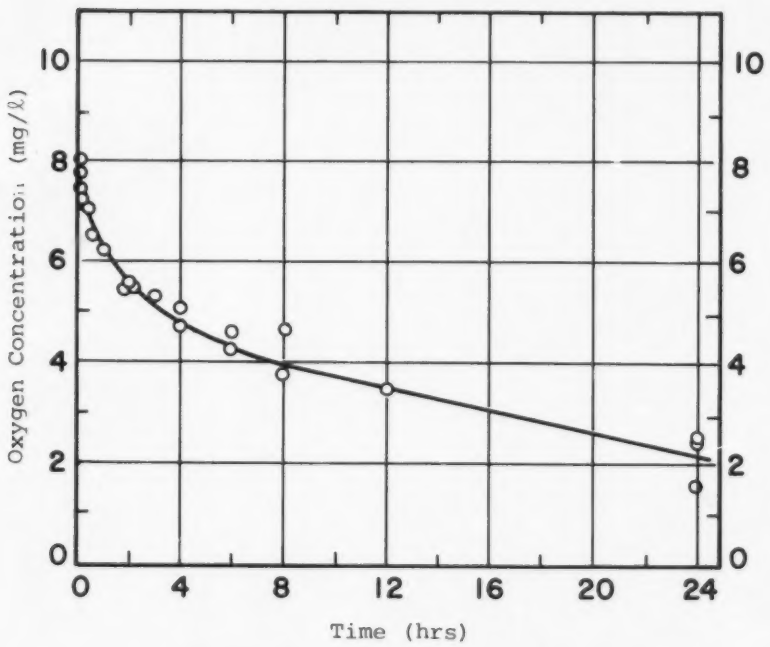

Figure 23. Oxygen Depletion Rate

after the coal has been separated. The residual turbidity will, of course, depend on the degree of efficiency of the separation process.

During the course of the experiment, it was observed that a slurry would separate when allowed to stand over a period of approximately one day. The supernatant above the coal particles was essentially clear, although some brownish hues were present. This occurrence was independent of slurry age. However, centrifuging the sample produced an entirely different supernatant. The water above the centrifuged cake was a dark brown color. Subsequent centrifuging did not result in observable increments of turbidity removal. Exact measurements were not made on the supernatant because it was felt that laboratory procedures used in slurry separation were not comparable to prototype slurry separating practices and that this experimental data should not be extrapolated.

In general, the observation was that more energy expended in separation produced more, not less, residual turbidity in the supernatant. Apparently, the rapid application of centrifugal forces on the slurry resulted in the finer, lighter fraction of the suspended coal being forced into the supernatant. In normal gravitational settling, however, these particles and colloids apparently became attached to and settled with the larger coal particles. Passing turbid supernatant water through a 0.45 μ filter resulted in a clear liquid, indicating that colloids or color molecules were greater than this size.

Oxygen Conditions

Assumptions are usually made that coal oxidizes in the presence of oxygen. This oxidation is assumed to occur both in air and in water containing free oxygen molecules (O_2). Thus, a slurry that initially contained dissolved oxygen would gradually move in an anaerobic conditions as the oxygen became depleted. Oxygen-initiated corrosion would, therefore, be a problem only in the first sections of the pipeline before oxygen depletion occurred. Similarly, aerobic biological and chemical reactions would occur in the initial length of the pipeline, and anaerobic biological and chemical conditions would occur in the remainder of the line.

Laboratory tests were made in an attempt to determine the rate of oxygen loss. A BOD bottle was filled with water and coal and an oxygen probe were placed in the bottle. The system was sealed so that aeration would not occur. Gentle agitation was provided by the impeller on the oxygen probe. It was necessary to use a mixture somewhat thinner than a 50-50 slurry to prevent fouling of the electrode membrane. A slurry consisting of approximately 40 percent coal was used. Figure 23 represents the oxygen content versus time for the system.

The fact that the oxygen content did not go to zero can be accounted for by two facts. First, the coal was dry ground in air and thus had been exposed to oxygen. An undetermined portion of its available oxidation sites could have already been utilized and second, because the amount of oxidizable surfaces would be in proportion to the amount of coal, a thicker suspension would have required more oxygen. Thus, a slurry of 50 percent solids would have required proportionally more oxygen.

In either event, it appears logical that oxygen depletion will occur under pipeline conditions. In most pipeline operations, it is anticipated that the coal will be wet ground and then slurried immediately so that all oxidation must rely on the oxygen in the mix water. This fact, coupled with the heavier coal loading in prototype pipelines, is almost certain to produce an anaerobic condition within a period of 24 hours or less.

ORGANIC PARAMETERS

Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organics and some inorganics in water. The COD test measures the amount of oxygen that would be consumed in biological oxidation reactions, plus the oxidation of biologically resistant organics that are susceptible to oxidation only under extreme conditions of heat, pH, and strong oxidants. There are some organic compounds (acetic acid, some aliphatic compounds, aromatic hydrocarbons, and so forth) that are not measured by the COD test.

The chemical oxygen demand test is subject to interferences by chlorides. Small quantities can be compensated for by the addition of mercuric sulfate. However, the large quantities of chlorides in the salt water of runs B3 and B4 prevented a valid COD test from being performed. Data for the freshwater runs are shown in Table 21 and Figure 24. Data for run B1 (freshwater run) indicates an initial drop and then a subsequent rise in the COD of the separated water. A similar pattern is shown in run B2 (friction and corrosion inhibitors added to fresh water) except that a considerable initial increase is shown prior to a decrease. A subsequent increase similar to that observed in run B1 is noted toward the end of the run.

One interpretation of this data would be that the oxidizable organics decrease during the initial stage of the run (possibly as a result of adsorption of oxidizable compounds in the mix water) and that oxidizable compounds are formed toward the latter stages of the runs. Obviously, oxidizable compounds are formed from the addition of the chemical friction and corrosion inhibitors. Too much significance should not be placed on this data, however, since the COD tests are not very accurate in this concentration range and the increase at the end of the run is not greatly significant. A more accurate assessment of the organics can be probably be obtained from the dissolved organic carbon (DOC) test described in the following section.

Dissolved Organic Carbon (DOC)

In addition to the inherent inorganic ions, transport water from a coal-slurry pipeline may contain organic matter that has been extracted from the coal. Presence of such material may be evidenced by elevated concentration of dissolved organic carbon (DOC)* and by color, odor, and taste. In this project, an examination of organic parameters was undertaken to(1) determine the DOC concentration of the water from coal-slurries relative to other parameters, and (2) characterize the DOC by solubility, phenol content, and high performance liquid chromatographic (HPLC) profiles.

Determination of DOC Concentration--

Samples of the transport water for determination of DOC concentrations were taken before introduction of the coal (mix water), shortly after the water was mixed with coal (0-hour), and at subsequent intervals. Each DOC determination is the average of triplicate analyses. These analyses are repeatable to within ± 0.5 ppm carbon. The data for four runs (B1, B2, B3, B4) are presented in Table 22 and appear graphically in Figure 25.

In studying the DOC levels within each run, it is apparent that, except for run B1, the DOC levels increased rapidly above background during the first six hours of a run. Thereafter, the DOC levels remained fairly constant or rose only slightly until the end of the run. In other words, it appears that most of the extractable organics are dissolved rapidly after contact with water. Therefore, if a

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*Organic material that will pass through a 0.45 μ filter.

TABLE 21 CHEMICAL OXYGEN DEMAND (mg/l)

Slurry Run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (days)	4 (days)	8 (days)	12 (days)
B1	3.4	11.1	8.8	ND	ND	<1	1.9	4.6	13.8
B2	14.6	39.6	48.5	42.7	33.8	19.8	18.8	24.0	30.4
B3	865	778	882	678	374	652	606	629	710
B4	473	567	499	470	336	458	413	600	630

ND = Not detectable

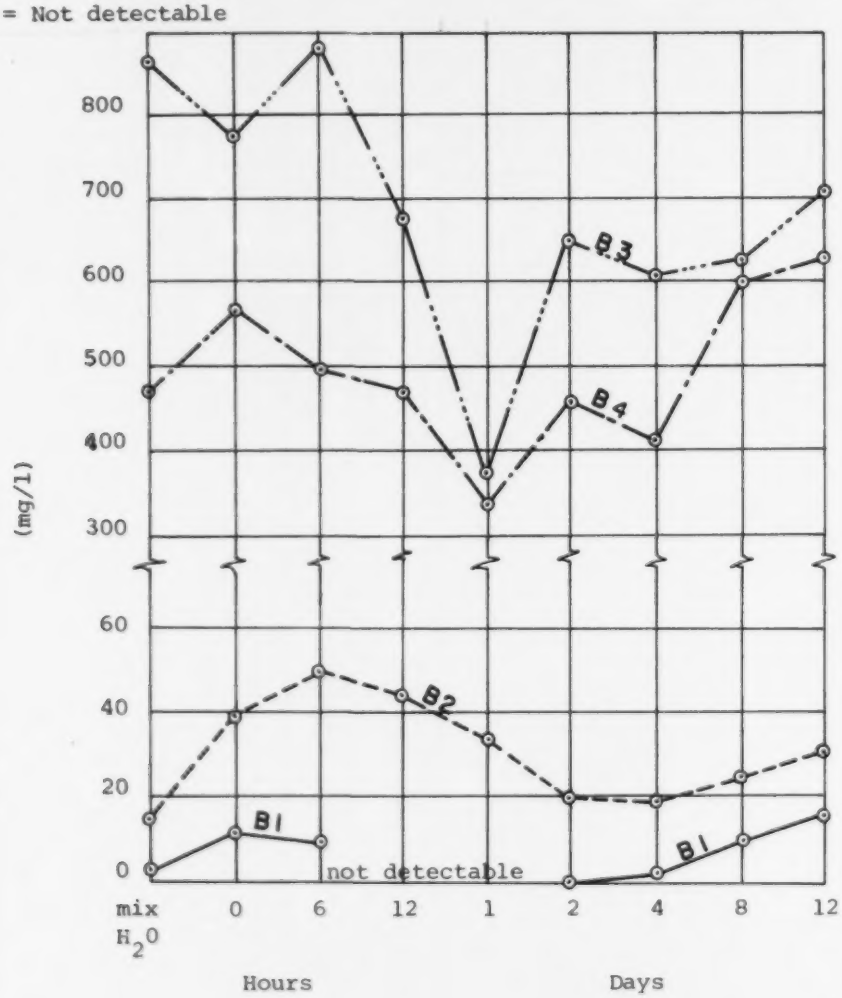

Figure 24. Chemical Oxygen Demand vs. Time

TABLE 22. DISSOLVED ORGANIC CARBON (DOC) (mg/ℓ)

Slurry run	Mix Water	Sampling Period 0 (hrs)	6 (hrs)	12 (hrs)	1 (day)	2 (day)	4 (day)	8 (day)	12 (day)
B1	26*	22	29	88*	24	63*	28	22	20
B2	5	15	18	19	20	19	22	-	24
B3	5	6	10	11	9	17	12	17	-
B4	2	8	-	-	12	16	21	14	14

*There is reason to suspect that these samples were improperly handled and are in error. These data were not used to draw any conclusions. The authors have confidence in the remaining data.

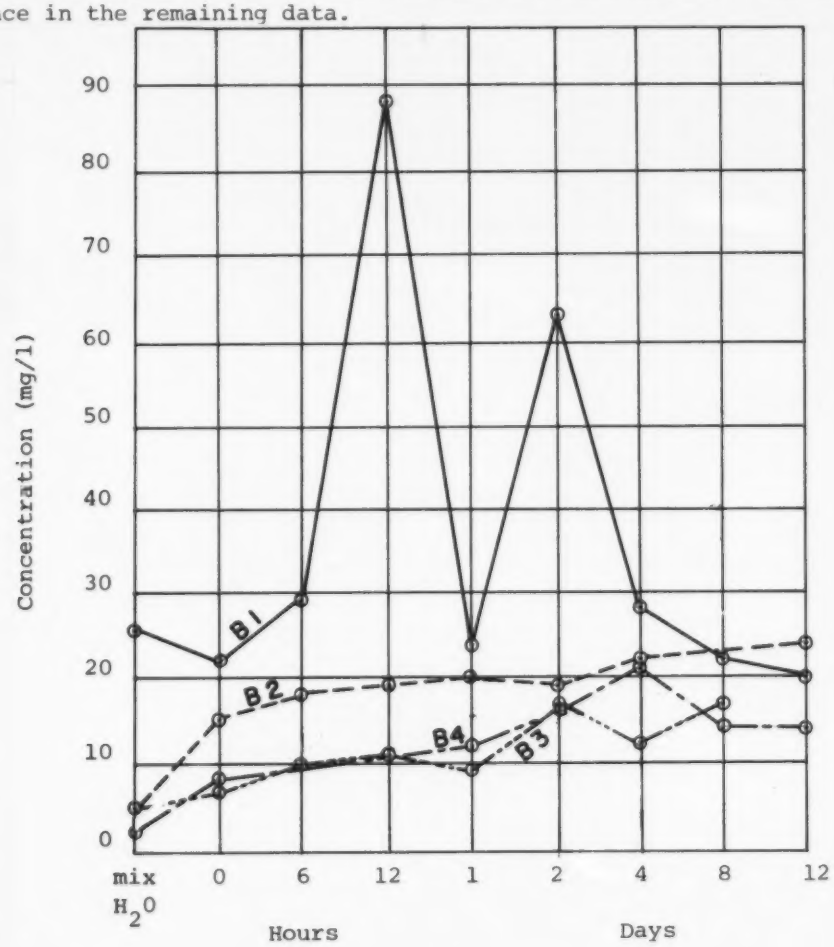

Figure 25. D O C vs. Time

run proceeded under normal conditions for at least six hours, the DOC levels at that point may be assumed to be reasonably indicative of the DOC levels which would have resulted from a normal run of 12 days' duration.

There is a certain amount of variability in the DOC values. Reasons for this are unknown, but may be partly related to problems with mixing or to small, unavoidable differences in sample handling, and so forth. Because this variability could not be eliminated, it is felt that the average value for DOC concentration from the 12-hour sample to the end of the run is the most useful value for these discussions.

In all of the runs, the average DOC concentrations were less than 25 ppm. The lowest value was 13.2 ppm in run B3.

It might be hypothesized that the DOC concentrations in the four runs would be similar because they were run in the same apparatus using the same coal and water source and without the addition of any organics. However, the results clearly show that the addition of salts and/or corrosion and friction-reducing agents reduces the amount of organic material dissolved. The DOC concentration in run B3, in which significant quantities of ionizing salts were used, is more than 40 percent less than that in run B1, in which no salts were added. It is reasonable to conclude that the lower DOC levels in these experiments were a result of saturation phenomena, analogous to the "salting out" process.

Because water-soluble organic compounds that are leached from coal contain polarizable or ionizable groups, the pH of the medium would be expected to influence the amount of organic material dissolved. Previous work at MSU has shown that there is indeed a relationship between the concentration of DOC and the pH of the extracting medium. The pH is a function both of the medium and of the coal since addition of coal to distilled water causes an immediate drop in pH. In this study, one objective has been to determine any correlation between the DOC concentration and pH of the coal-slurry transport water and those parameters from laboratory test leachates.

Figure 26 contains plots of DOC concentration against pH for each of three systems, one buffered with phosphate, one with borate, and a third unbuffered. Each point represents a sample containing 1 ℓ of the specific buffer and 100 g of 50-100 mesh coal, maintained at the pH given and shaken for 9 days. The aqueous portion was then analyzed for DOC. There is a strong trend for the amount of carbon extracted to increase with pH. The nature of the buffer has no effect.

Table 23 gives average DOC and pH data. These data compare well with data in Figure 26. It is the opinion of the writer, however, that high salt concentrations will override the effect of pH. Therefore, the laboratory curve may be used as a predictive tool for coal-slurry transported in normal, non-saline water.

TABLE 23. pH AND AVERAGE DOC

Slurry run	DOC (mg/ℓ)	pH (units)	Slurry variables
B1	24	6.2	Fresh water – no additives
B2	20	6.0	Fresh water – additives
B3	13	6.1	Saline water – no additives
B4	15	6.1	Saline water – additives

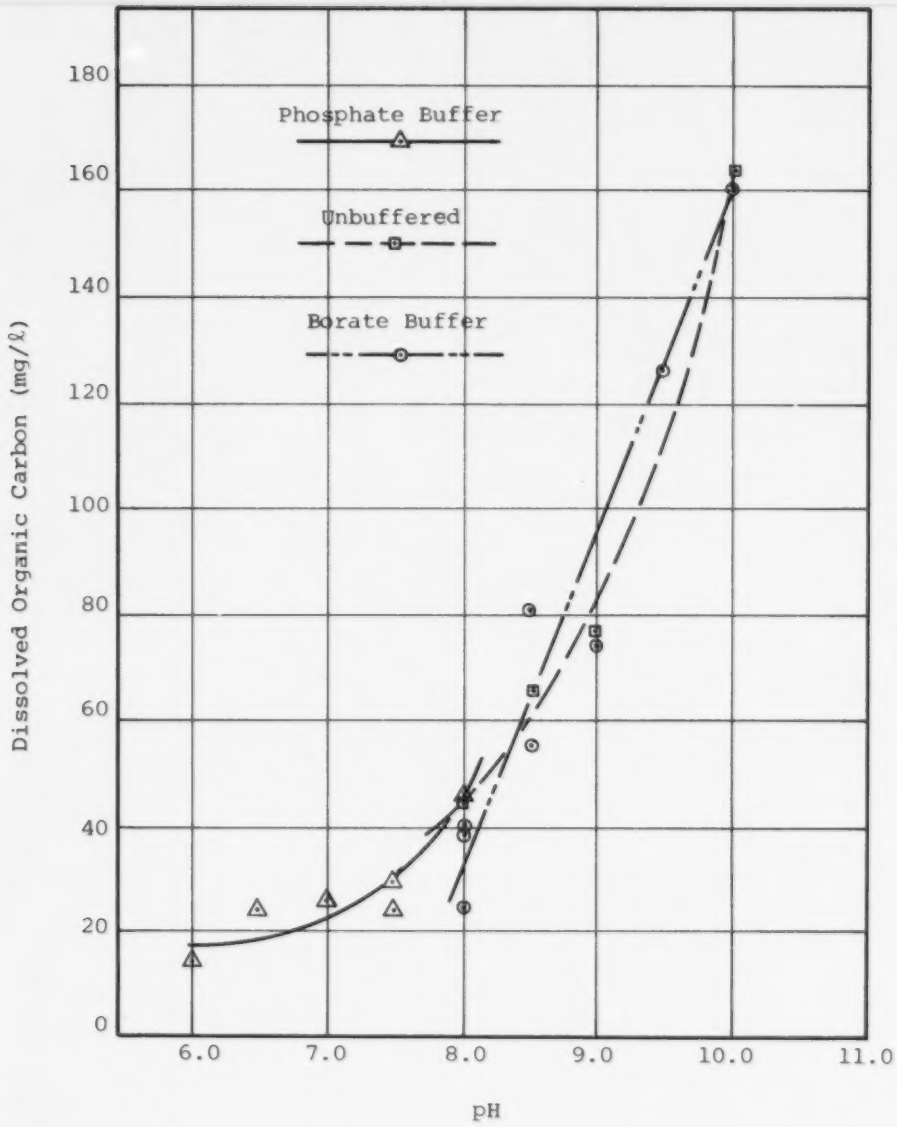

Figure 26. Dissolved Organic Carbon vs. pH

Previous work by Jennings (1979) has shown that water percolating through a coal seam aquifer does not, in general, dissolve large amounts of organic materials. It would seem that increasing the surface area by decreasing the particle size of the coal should increase the amount of DOC extracted. It is now known that this is true to a certain extent, as shown in Table 24. As much as 6.8 ppm of DOC may be extracted from a stirred sample with coal sizes between 0.150 and 0.300 mm. When the particle sizes are smaller than 0.150 mm, however, the DOC level drops off. It seems that, while coal particle size is a factor to be considered in predicting the amount of organic material to be extracted in a coal slurry, it is probably not an overwhelming factor.

TABLE 24. EFFECT OF COAL PARTICLE SIZE ON EXTRACTABLE ORGANICS

Coal size	DOC extracted, ppm
3-12.5 mm	5.0
1.4-3.0 mm	5.4
0.150-0.300 mm	6.8
0.075-0.150 mm	4.2

If dissolved organic materials are preceived to be a problem in water from coal mines, coal-slurry pipelines and so forth, more definitive models of characterizing these materials will be needed. Two approaches to the problem are discussed below: (1) characterizing DOC by phenol content, and (2) characterizing DOC by means of HPLC.

Phenol content--When studying organic pollutants of aqueous systems, phenol content is often determined. Phenols are important for several reasons: they are common, they are toxic, and they are difficult to remove. The extent to which organic compounds extracted from coal might contain phenolic groups is not known. The purpose of this portion of our work was to determine whether or not phenolic groups were present in the transport water of a coal-slurry system.

A colorimetric test, the Folin-Ciocalteu Determination, may be used to analyze an aqueous sample for phenol content. An absolute concentration of phenol can be calculated using a system of standards. In this work, however, the exact nature of the phenol-containing moieties is not known. Therefore, it is feasible to express the phenol content in only relative terms, i.e., as absorbance per part-per-million DOC.

Figure 27 shows some relationships between absorbance at 720 nm for Folin-Ciocalteu test solutions and their carbon contents. Tyrosine, a phenolic compound, is compared with humic acid (which is assumed to contain 60 percent carbon) and fulvic acid (which is assumed to contain 50 percent carbon). Also plotted are two points that represent the average absorbances and DOC concentrations for each of two preliminary tests. From this figure it can be seen that the phenol content of the DOC in transport water is quite low when compared with humic or fulvic acid at the same carbon concentration. It should be noted that the organics in coal-water systems should be described as fulvic acids because they are soluble in water at pH 2.

HPLC profile--While the measurement of DOC concentration can give an investigator some information on the quantity of organic materials in the water used as transport medium in a slurry system, it cannot provide data on the different types of carbon compounds present in that water. For volatile organic components, gas chromatography may be used. However, for nonvolatile compounds, that method is not effective. Because high performance liquid chromatography (HPLC) has shown promise in such analyses, it was used in this project.

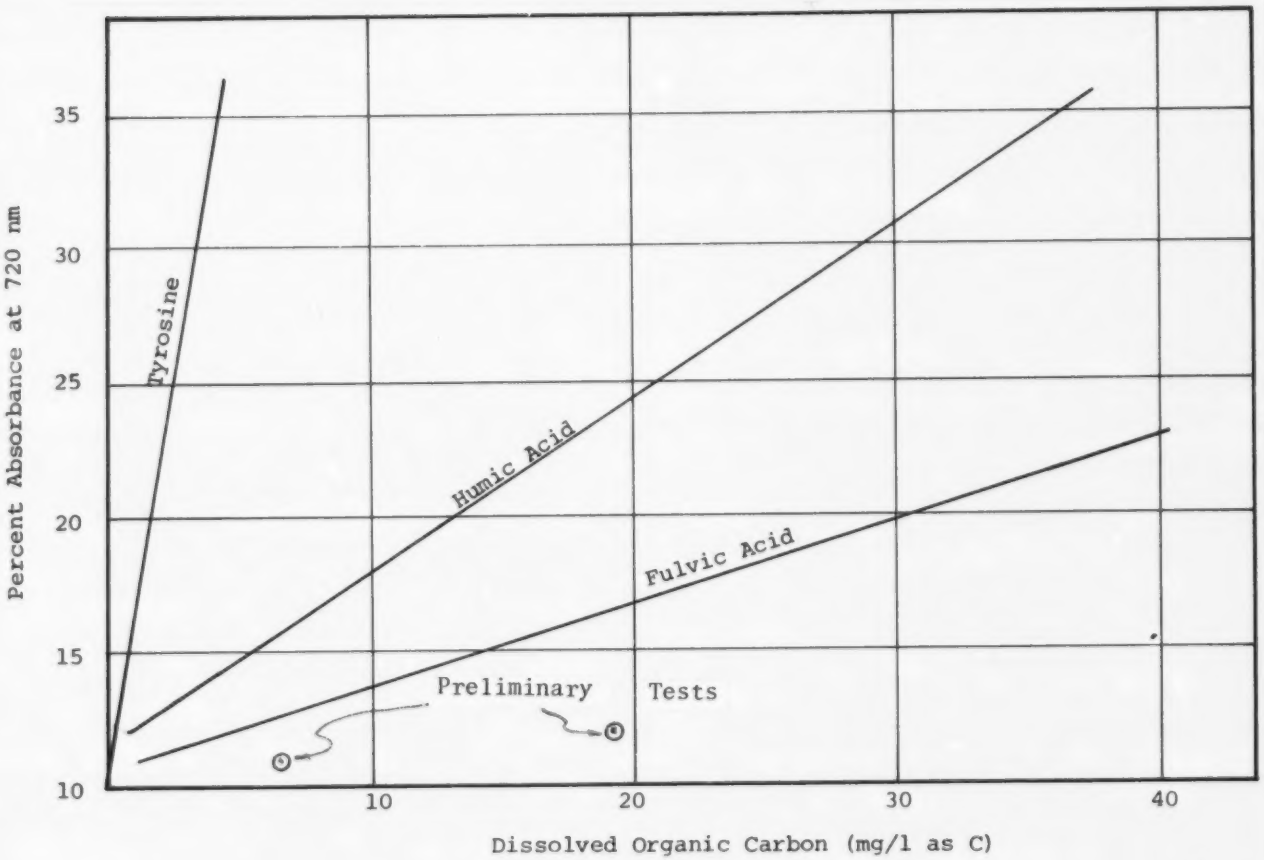

Figure 27. Dissolved Organic Carbon vs. Absorbance

The HPLC system used permits the separation of the organic components in water according to their affinity for the hydrophobic C_{18} chains in the HPLC column packing. In samples such as those obtained in this study, affinity HPLC will not permit separation and identification of individual organic components because the mixtures of organics are very complex and the differences from component to component may be small. However, HPLC does yield a profile, a "fingerprint," which is characteristic of the source of the DOC. In this profile, less hydrophobic materials elute first and appear on the left of the chromatogram; more hydrophobic materials elute later and appear on the right. The HPLC profiles of several samples may, therefore, be used to demonstrate the differences among DOC materials arising from various sources and under the various experimental conditions of this project.

As has been discussed, DOC has commonly been divided into two broad classes, namely humic and fulvic acids. Figure 28 shows the HPLC profiles of humic and fulvic acids extracted from coal at pH 12. The third trace on this figure is that of a natural DOC material that was obtained from a water well in Eastern Montana. This well was recharged from an aquifer in Leonardite, an oxidized form of coal. Based upon the acid precipitation method, this natural DOC material would be classified as fulvic acid. However, its HPLC profile clearly shows that it is not the same as the fulvic acid derived from coal; neither is it directly comparable to the humic acid. The fulvic acid contains more hydrophilic and the humic acid contains more hydrophobic materials than the natural DOC.

Figures 29, 30, 31, and 32 show the HPLC profiles of DOC from the 12-day samples of the four runs. (Data for concentrations of DOC were given in Table 22.) From these profiles, it is apparent that the nature of the DOC in each experiment is somewhat different. A broader spectrum of compounds was extracted when friction reducer and oxygen scavenger were present in the transport water (runs B2 and B4) than in the other experiments. Water containing high salt concentration (run B3) extracted nearly the same type of DOC as water with no additives (run B1). In run B4, with both high salt concentration and friction reducer/oxygen scavenger present, the chromatograph shows the expected combination of effects.

CHANGES IN COAL QUALITY

The primary effort in the experimental phase of the project was to determine changes in the transport water quality. In addition, an effort was made to document corresponding changes in coal quality. Samples were taken from batches of coal prior to slurrying, and additional samples were taken from the coal after slurry separation. An analysis was made by Chemistry Station Analytical Lab at MSU on both samples for most of the parameters for which the water was tested plus several other parameters not covered in the water samples. Data from these measurements, along with available data from before and after water samples for comparison, are shown in Table 25.

A great many inconsistencies can be observed in the data in Table 25. It was anticipated that water quality would deteriorate and the solid coal would lose contaminants. While this is generally the case, some notable and unexplainable occurrences can be seen. For instance, chromium and copper increased in the coal while decreasing in the water (except for run B3 where this was reversed); lead content of the coal showed a little increase in the salt water runs (B3 and B4), but decreased in the fresh water (B1 and B2). Occasional unexplained spikes appear in the data, such as chromium in the 12-day coal for runs B2 and B4 and nickel in the 12-day coal for run B4. These spikes are an order of magnitude and were confirmed by repeated analysis of the same sample.

It is immediately apparent that a mass balance of the trace elements in the coal cannot be made using the data in Table 25. The most logical explanation of the lack of consistency of the data is

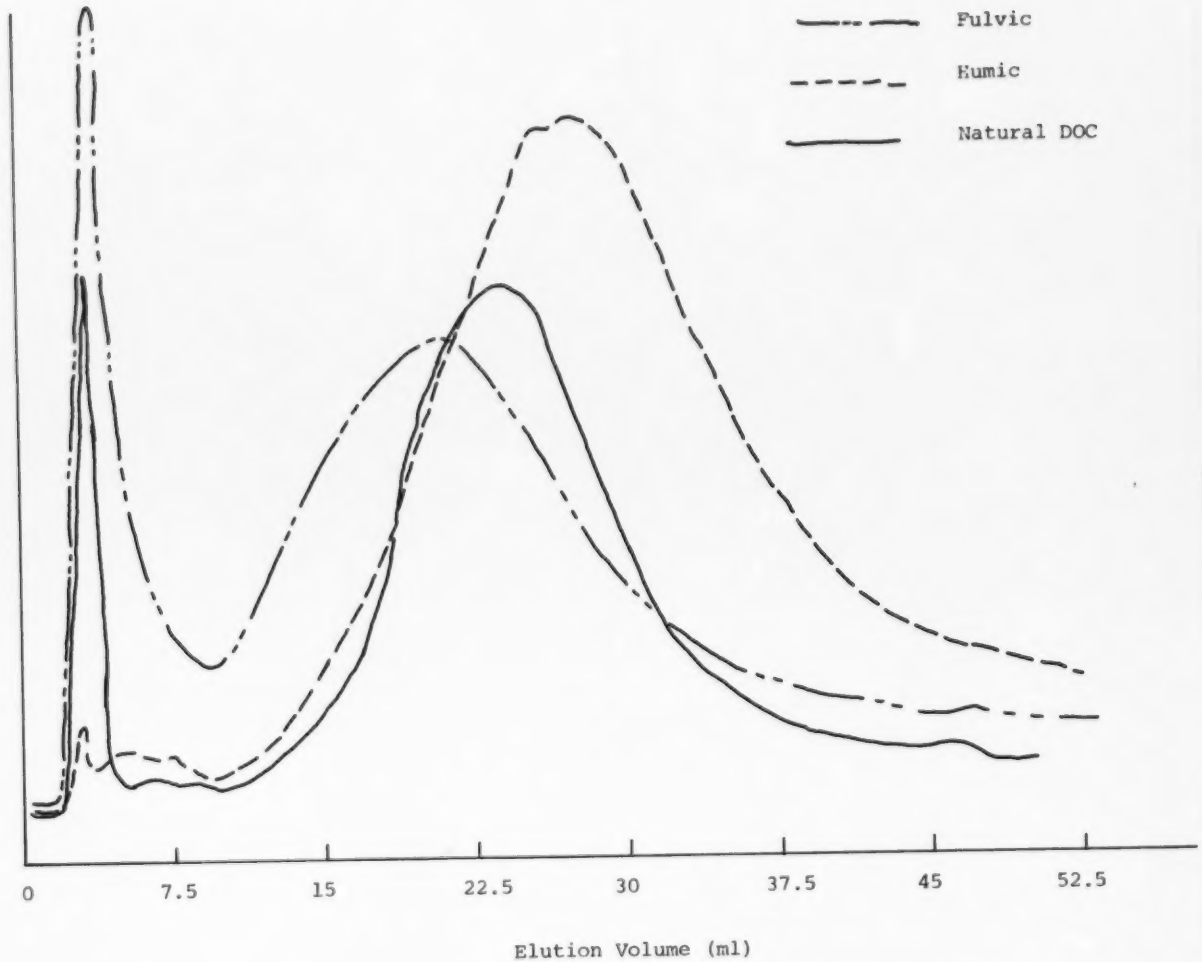

Figure 28. HPLC Profiles of Humic and Fulvic Acids and Natural DOC Materials

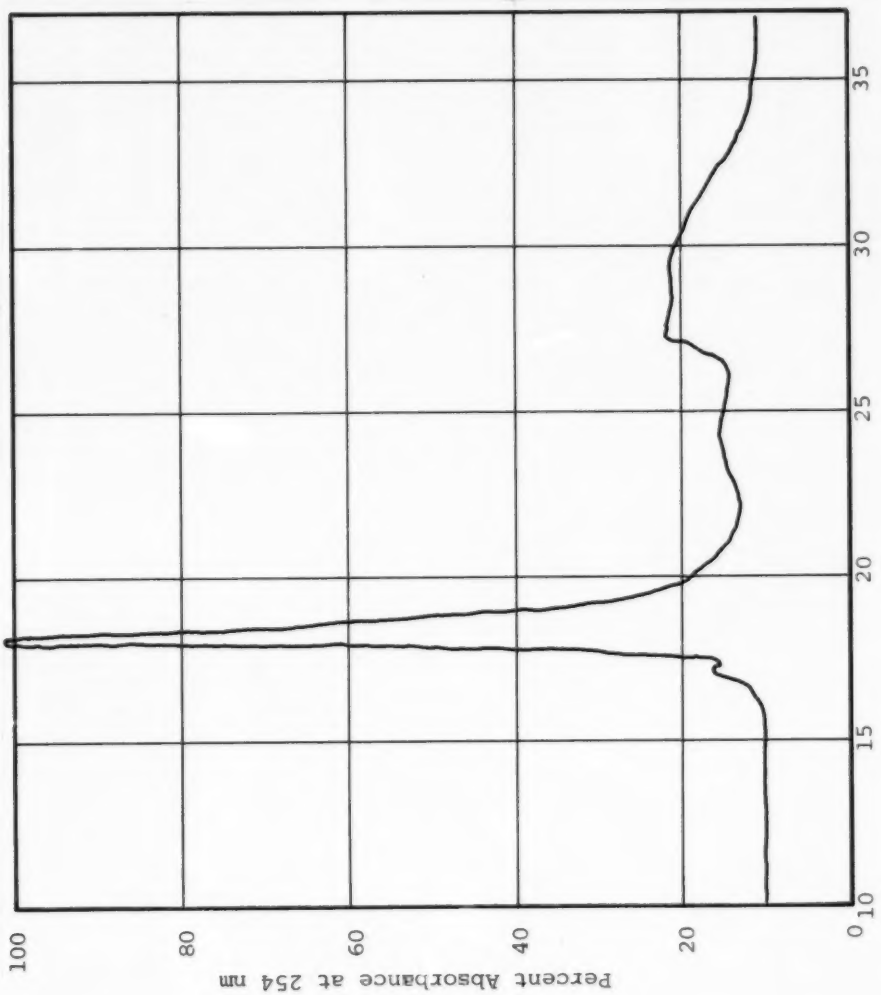

Figure 29. HPLC Profile for Run No. B1

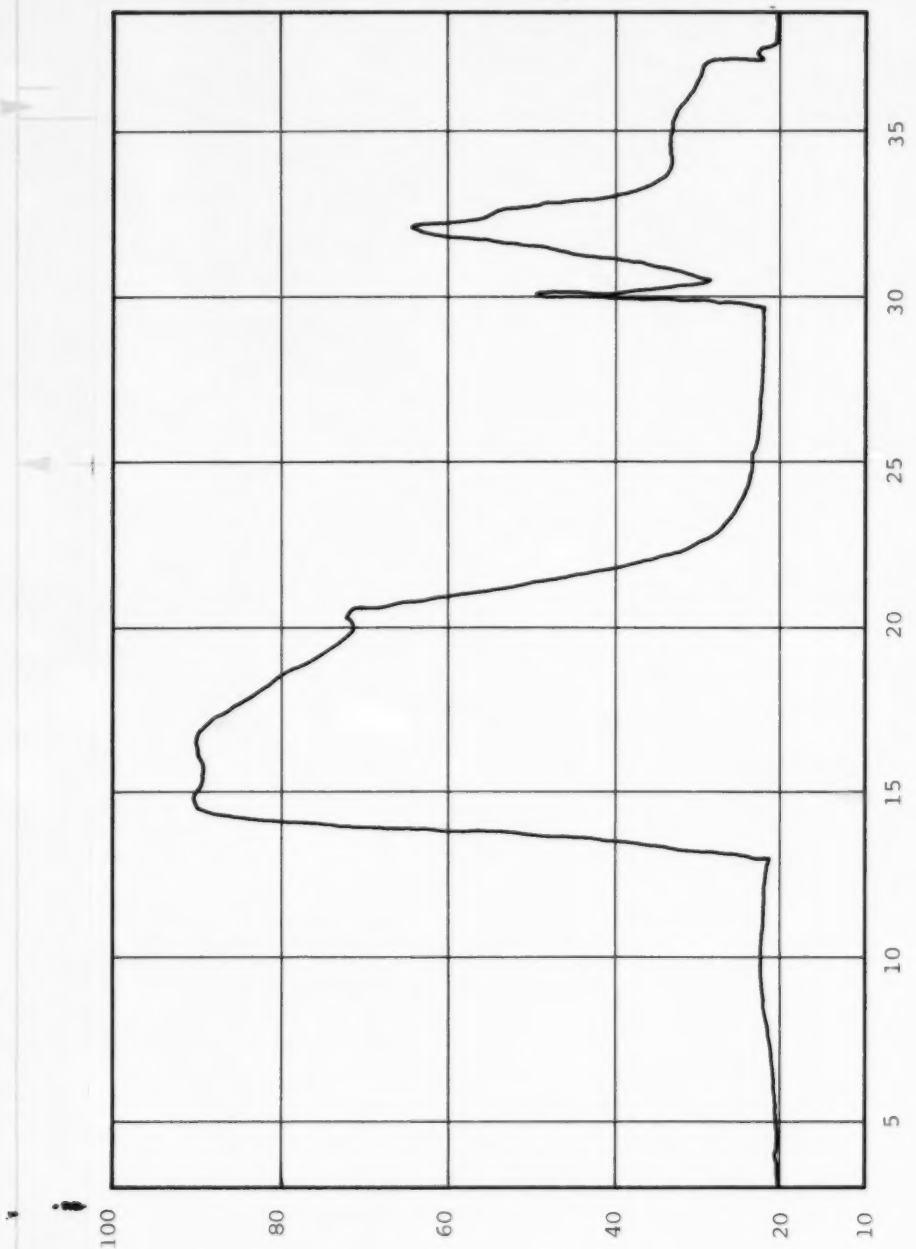

Figure 30. HPLC Profile for Run No. B2

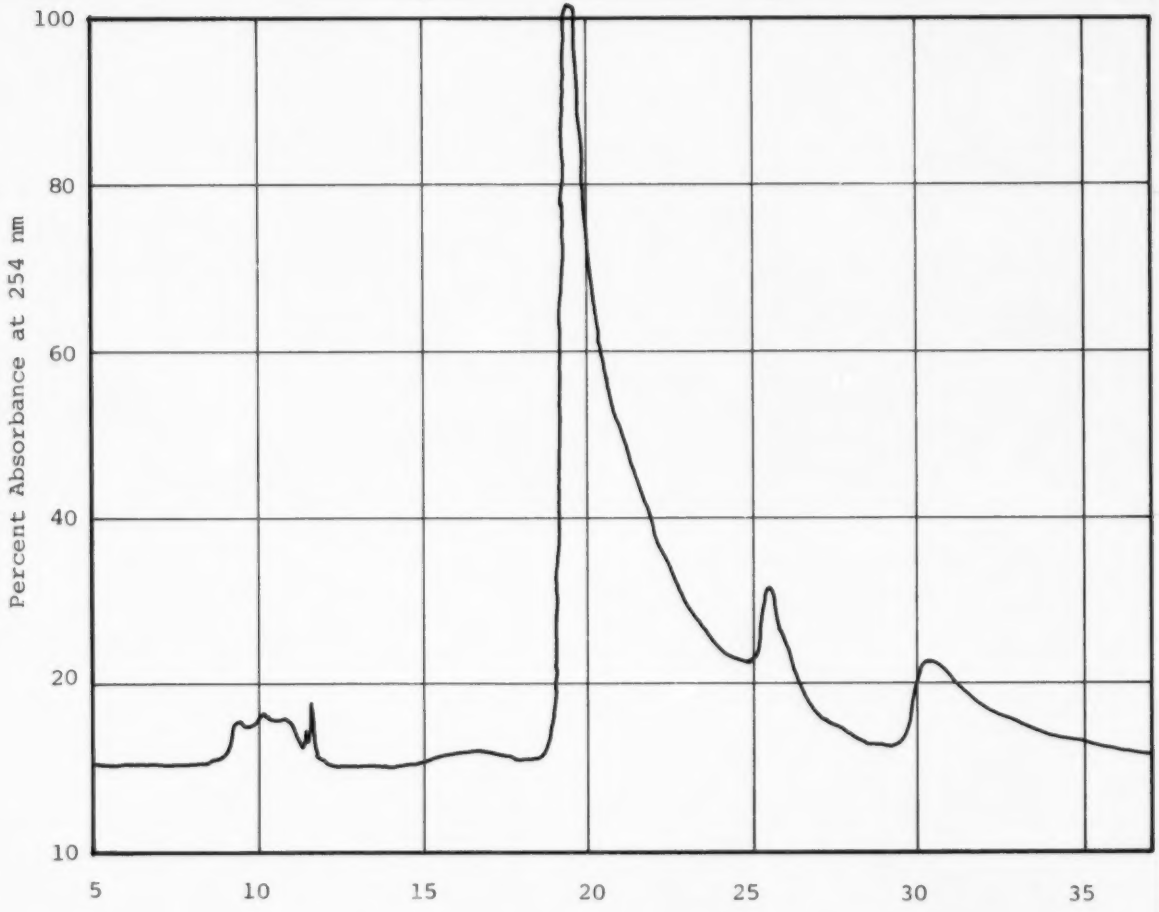

Figure 31. HPLC Profile for Run No. B3

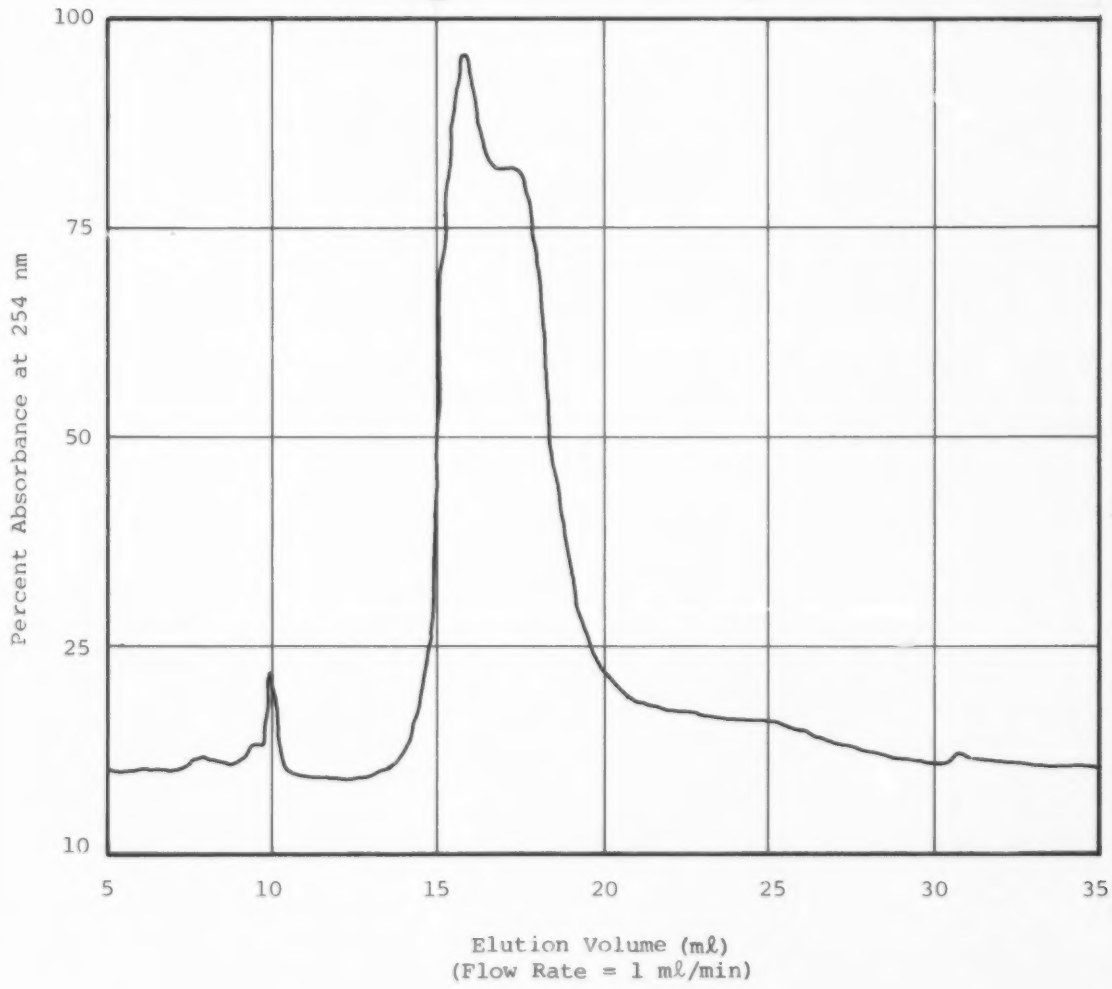

Figure 32. HPLC Profile for Run No. B4

TABLE 25. ANALYSIS OF WATER AND COAL BEFORE AND AFTER 12 DAY CONTACT

PARA-METER	RUN B1				RUN B2				RUN B3				RUN B4			
	Pre-mix Water	12-day water	Pre-mix coal	12-day coal	Pre-mix water	12-day water	Pre-mix coal	12-day coal	Pre-mix water	12-day water	Pre-mix coal	12-day coal	Pre-mix water	12-day water	Pre-mix coal	12-day coal
Arsenic	0.011	0.026	5.17	4.34	0.014	0.073	4.35	2.85	0.012	0.027	5.08	4.66	0.006	0.08	3.95	2.0
Chromium	0.001	0.001	8.8	9.4	0.001	0.088	12.4	500	0.093	0.067	5.13	1.93	0.006	0.007	28.6	133
Copper	0.07	0.03	5.4	6.1	0.16	0.04	11	18	0.48	0.07	8.3	7.2	0.18	0.08	12	18
Lead	0.006	0.045	18.2	14.1	0.006	0.045	9.15	4.91	0.038	0.030	7.33	12.99	0.02	0.015	3.95	5.4
Manganese	< 0.01	0.66	142	123	<0.01	0.85	160	120	0.04	4.36	97	68	0.01	3.84	120	130
Mercury *	0.74	0.30	0.39	0.019	0.24	0.43	0.035	0.035	0.78	0.29	0.027	0.012	1.54	0.93	0.10	0.06
Nickle	0.005	0.005	6.9	4.7	0.005	0.005	14.8	0.275	0.01	< 0.01	19.54	3.0	0.01	0.013	24.7	226
Zinc	0.02	0.04	4.9	3.8	0.04	0.09	11	28	0.10	0.74	5.6	3.3	0.55	0.24	23	35
Fluoride	--	--	0.002	0.002	--	--	34	20	--	--	19	22	--	--	43	19
Sodium	--	--	--	--	142	248	330	350	9,080	7,300	189	4030	9,250	6,125	220	3300
Chloride	4.12	5.0**	207	25	4.2	6.3	350	460	15,200	13,600	1.6	27	12,900	12,600	350	2040
Sulfur***	--	--	0.73	0.25	--	--	0.55	33	--	--	0.61	0.39	--	--	0.58	0.36
Calcium***	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.92	0.71
Magnesium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.33	0.16
Phosphorus	--	--	--	--	--	--	--	--	0	27	0.175	0.056	0	32	0.15	0.019

* parts per billion
** 4 day sample
*** %

NOTE: coal data in terms of mg/kg

water data in terms of mg/l

the known inconsistency of the composition of the coal. As noted in the previous sections of this report, coal varies in quality both vertically and horizontally in the coal seams. In all likelihood, this variability also extends to the micro scale. While the coal used in this experiment may have come from the same power shovel scoop at the mine and later received considerable mixing and homogenizing during grinding operations, still it is probable that any two small aliquots taken from a larger sample will be quite variable in quality. (This is evidenced by the range of values observed in the pre-mix coal for the four runs.) Thus, samples of a gram or so each taken before and after each run would be expected to show considerable variability. It is this writer's opinion that to perform a mass balance between constituents of the coal and the water, extensive effort would be required to homogenize the coal prior to slurrying and to run many duplicate samples on both the premix and 12-day coal. Perhaps the averages of these samples would then be representative of before and after conditions. Time and money constraints prevented this type of analysis in this experiment.

One very useful bit of information is apparent in Table 25. The data clearly indicate that sodium and chloride from the salt water runs either adsorb to the coal or precipitate, and are removed with the coal during slurry separation.

This phenomenon could have serious consequences if saline water is used as a transport medium. The increased minerals would result in larger volumes of fly ash and the sodium and chloride would cause corrosion problems in power plant equipment.

SECTION 7

POSSIBLE TREATMENT SYSTEMS FOR TRANSPORT WATER

The nature and extent of treatment of transport water will, of course, depend upon many factors. These include the characteristics of the water before slurrying, the chemical additives used for friction and corrosion control, the nature of reuse, dilution by other waters or wastewaters, and the conditions of final discharge.

The initial characteristics of the slurry water are quite important. While fresh water becomes contaminated to some extent, a modest amount of conventional treatment will render the transport water fit for some uses in the power plant operations, or for discharge to ambient water courses. If salt water is used, however, extensive operations will be necessary before reuse is practical or discharge possible. (A possible exception would be discharge to the ocean or other salt water bodies with which the dissolved material would be compatible.) Saline water would have little use, even for cooling water, in power plant operations, and would be extremely difficult to treat to an acceptable quality for discharge to fresh water. Chemical precipitation of dissolved solids would not be very effective if large quantities of sodium were present, and selective membrane filtration (reverse osmosis or electrodialysis) would be problematic and expensive at high concentrations of TDS. Additional problems with salt water include corrosion of pipelines and other elements of the slurry systems and corrosion of combustive elements at the power plant. Since coal, or other material associated with the coal, appears to absorb sodium and possibly other materials from the salt water, an increase in fly ash production should be expected. Washing of the coal with fresh water prior to firing might alleviate some combustion problems.

For initially fresh transport water the nature of the reuse will determine the treatment process. Unless only poor quality water is available locally, it is doubtful that slurry water will be treated and used for boiler water at the power plant. Because the separated water will constitute only a small percentage (probably about 25 percent) of the total water needed for cooling purposes, it is possible that the transport water could be diluted and used directly with no treatment other than turbidity removal. To prevent solids build-up in recirculated cooling water systems, it may be necessary to precipitate some of the solids.

For simple discharge to surface waters, turbidity removal only would probably be sufficient for initially fresh transport water. Coagulation with ferrous or aluminum salts, possibly with the addition of polymers, followed by flocculation and settling should produce an effluent of sufficient quality for discharge.

The effects of the organic quality on reuse and discharge should receive special consideration. While the organics are not present in sufficient quantity, and are probably not sufficiently biodegradable to cause dissolved oxygen problems in receiving waters, a problem may arise if the transport water is chlorinated. It is known that many organics that are associated with derivatives from fossil fuels are precursors of chlorinated hydrocarbons, many of which are known or suspected carcinogens. It is not known at the present time if the dissolved organics in transport water will react with chlorine to form potentially dangerous compounds, but considering the probable nature

of the organics (humic or fulvic acids) it is likely that some undesirable compounds will be formed by the addition of chlorine. This could be a significant point in reuse as cooling water since it is a common practice to chlorinate to prevent biological films from growing on exposed surfaces in the cooling systems.

Should future work establish that precursors of chlorinated hydrocarbons do exist in slurry transport water, two courses of action are available: (1) use a biocide other than chlorine, or (2) remove the objectionable material prior to contact with chlorine.

Removal of dissolved organics can be accomplished by activated carbon treatment. (While activated carbon can be manufactured from coal, it should be noted that coal as found in the slurry will not act as an activated carbon material unless first processed appropriately.) Activated carbon treatment can be accomplished by the addition of powdered activated carbon to the water after coal separation and subsequently removing the material by settling and filtration processes. Another method would be to filter the transport water through a bed of granular activated carbon. This process is usually more effective than the use of powdered activated carbon but would require clarification and probably filtration to remove solid material before to granular activated carbon filtration.

Although cost analysis is beyond the scope of this report, it is obvious that removal of dissolved organic material would present a substantial increase in the cost of treating transport water.

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APPENDIX A

Solubility of Metals and Metal Compounds

Elemental Form		Chloride Form		Oxide Form	
	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)
Antimony (Sb)	insoluble	$SbCl_5$	decomposes	Sb_2O_5	very slightly
		$SbCl_3$	601.6 (0°C) ∞ (80°C)	Sb_2O_4 as cervantite	very slightly
				Sb_2O_3 as valentinite or senarmontite	very slightly
Arsenic	insoluble	$AsCl_3$	decomposes	As_2O_3	3.7 (30°C)
				As_2O_3 as arsenolite or claudetite	1.2 (2°C)
				As_2O_5	150 (16°C)
Beryllium (Be)	insoluble (decomposes in hot H_2O)	$BeCl_2$	very sol.	BeO as bromellite	$2x10^{-5}$ (30°C)
				$BeO \cdot X\ H_2O$	insoluble
Cadmium (Cd)	insoluble	$CdCl_2$	140 (20°C)	CdO	insoluble
		$CdCl_2 \cdot 2\text{-}1/2H_2O$	168 (20°C)		
Chromium (Cr)	insoluble	$CrCl_2$	very sol.	CrO_2	insol.
				CrO	insol.
		$CrCl_3$	insol.	Cr_2O_3	insol.
				CrO_3	61.7 (0°C)
Copper (Cu)	insoluble	CuCl as nantokite	0.0062	Cu_2O	insol.
		$CuCl_2$	70.6 (0°C)		
		$CuCl_2 \cdot 2H_2O$	110.4 (0°C)	CuO	insol.
		$CuCl \cdot 3[CS(NH_2)_2]$	very sol.		

APPENDIX A (CONT.)

Elemental Form		Chloride Form		Oxide Form	
	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)
Fluorine (F)	$\rightarrow HF+O_3$	--		F_2O	slightly sol. may decompose
Germanium	insoluble	$GeCl_2$	decomposes	GeO_2 in tetrahedral crystal	insoluble
		$GeCl_4$	decomposes	GeO_2 in hexagonal crystal	0.447 (25°C)
				GeO	insoluble
Lead (Pb)	insoluble	$PbCl_2$ as cotunite	0.99 (20°C)	PbO_2	insoluble
				PbO as litharge	0.0017 (20°C)
				PbO as massicot	0.0023 (22°C)
		$PbCl_4$	decomposes	Pb_3O_4	insoluble
				Pb_2O_3	insoluble
				Pb_2O	insoluble
Manganese (Mn)	decomposes	$MnCl_2$ as scacchite	72.3 (25°C)	Mn_3O_4	insoluble
		$MnCl_2 \cdot 4H_2O$	158 (8°C)	MnO	insoluble
				Mn_2O_7	very sol.
				MnO	insoluble
				Mn_2O_3	insoluble
				MnO_3	soluble
Mercury (Hg)	insoluble	Hg_2Cl_2	0.0002 (25°C)	Hg_2O	insoluble
		$HgCl_2$	6.9 (20°C)	HgO	0.0053 (25°C)

APPENDIX A (CONT.)

Elemental Form		Chloride Form		Oxide Form	
	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)	Compound	Solubility (g/100 ml)
Nickel (Ni)	insoluble	$NiCl_3$	64.2 (20°C)	NiO	insoluble
		$NiCl_3 \cdot 6H_2O$	254 (20°C)		
Selenium (Se)	insoluble	Se_2Cl_2	decomposes	SeO	38.4 (14°C)
		$SeCl_4$	decomposes	SeO_3	ver sol., decomposes
Zinc (Zn)	insoluble	$ZnCl_2$	432 (25°C)	ZnO as zincite	1.6×10^{-4} (29°C)
				$ZnO_2 \cdot 1/2H_2O$	decomposes

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